

SURFACE BRILLOUIN SCATTERING IN OPAQUE THIN FILMS AND BULK MATERIALS

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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before any degree or examination in any other University.

A handwritten signature in blue ink, appearing to read 'S. Beyer', is written over a horizontal line.

(Signature of Candidate)

26 Day of OCTOBER 2012

Abstract

Room temperature elastic properties of thin supported TiC films, deposited on silicon and silicon carbide substrates and of single Rh-based alloy crystals, Rh_3Nb and Rh_3Zr , are investigated by the Surface Brillouin Scattering (SBS) technique.

Velocity dispersion curves of surface acoustic waves in TiC films of various thicknesses, deposited on each substrate (Si and SiC) were obtained from SBS spectra. Simulations of SBS spectra of TiC thin hard films on germanium, silicon, diamond and silicon substrates have been carried out over a range of film thickness from 5 nm to 700 nm. The simulations are based on the elastodynamic Green's functions method that predicts the surface displacement amplitudes of acoustic phonons. These simulations provide information essential for analysis of experimental data emerging from SBS experiments. There are striking differences in both the simulated and experimental SBS spectra depending on the respective elastic properties of the film and the substrate. In fast on slow systems (e.g. TiC on silicon), the Rayleigh mode is accompanied by both broad and sharp resonances; in slow on fast systems (e.g TiC on SiC), several orders of Sezawa modes are observed together with the Rayleigh mode. The velocity dispersion of the modes has been obtained experimentally for both situations, allowing the elastic constants of the films to be determined. Effects of two deposition conditions, RF power and substrate bias, on the properties of the films are also considered.

Platinum metal group alloys are promising candidates for future ultra high temperatures gas turbines materials due to their excellent high-temperature properties. In the present work, room temperature elastic properties of single crystals of Rh_3Nb and Rh_3Zr are investigated. SBS spectra for a range of wave vector directions from the (001) surface have been acquired in order to determine the angular variation of the surface acoustic wave velocities and the longitudinal wave threshold within the Lamb shoulder. The elastic stiffnesses of the specimens were determined using two approaches; one approach involves a least-square fit of the experimental data to calculated results and the other is an analytical approach which involves the χ^2 minimization of secular equations for the Rayleigh surface acoustic wave and the longitudinal wave threshold velocities in the [100] and [110] directions on the (001) surface of a cubic crystal. Results from the two methods were in good agreement.

To My Parents...

Pediya Muchenje and *the late* Obert Saidi Sumanya

*NDINOTENDA, ZIKOMO, TWALUMBA
NERUDO NEKUTSUNGIRIRA KWENYU, UKO KWANDIPA KUTI
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Contents

Abstract	iii
Acknowledgements	vi
Contents	viii
List of Figures	xii
List of Tables	xviii
1. Introduction	1
1.1 Background.....	1
1.2 Elasticity	2
1.2.1 Stress and strain	3
1.2.2 Hooke's law	4
1.2.3 Engineering moduli	8
1.3 Techniques for studies of elastic properties	9
1.3.1 Brillouin scattering and surface Brillouin Scattering	9
1.3.2 Ultrasonic methods.....	12
1.3.3 Inelastic neutron scattering and X-ray scattering	12
1.3.4 Resonance methods	13
1.3.5 Scanning acoustic microscopy (SAM).....	14
1.4 Thin supported films (TiC films)	14
1.5 Bulk materials (platinum group alloys)	17
1.6 Outline of the present work	18
2. Brillouin and Surface Brillouin Scattering	20
2.1 Introduction	20
2.1.1 Scattering mechanisms	22
2.1.2 Stokes and anti-Stokes bands	23
2.2 Brillouin scattering	24

2.2.1 The Brillouin tensor.....	25
2.2.2 Brillouin scattering in transparent solids.....	27
2.3 Surface Brillouin scattering.....	30
2.3.1 Conservation laws	30
2.3.2 Kinematics of surface Brillouin scattering	31
2.3.3 Scattering cross section for the ripple mechanism.....	32
2.4 Elastodynamic Green's function method	34
2.4.1 Bulk waves.....	35
2.4.2 Surface waves	37
2.4.3 Green's function for the surface of a bulk solid.....	40
2.4.4 Green's function for the surface of an opaque film	45
3. Experimental arrangement	50
3.1 Introduction	50
3.2 Laser.....	52
3.2.1 Emission and absorption	52
3.2.2 Laser design	53
3.2.3 Argon ion laser	55
3.2.4 Intra-cavity etalon	56
3.3 Auxiliary optics	59
3.4 Tandem Fabry-Pérot Interferometer	61
3.4.1 Introduction to Fabry-Pérot Interferometry	61
3.4.2 The Tandem Fabry- Pérot Interferometer (TFPI).....	66
3.4.3 Design of the scanning TFPI.....	68
3.4.4 Vibration isolation and stabilization	69
3.5 Experimental aspects.....	71
3.5.1 Daily set up for SBS measurements	71
3.5.2 Data capture and analysis	71

4. SBS Theory of a Supported Titanium Carbide Film	73
4.1 Introduction	73
4.2 Calculations of elastic stiffnesses of TiC films using Voigt, Reuss and Hill methods	76
4.2.1 Transformation of elastic stiffness and compliances	77
4.3 Fast on slow system	82
4.3.1 Acoustic behaviour for a strongly stiffened situation (<i>TiC/Ge</i>)	83
4.3.2 Acoustic behaviour for a weakly stiffened situation (<i>TiC/Si</i>)	86
4.4 Slow on fast system	90
4.4.1 Acoustic behaviour for a strong loading system (<i>TiC/diamond</i>)	90
4.4.2 Acoustic behaviour for a weak loading system (<i>TiC/SiC</i>)	93
4.5 Concluding remarks	96
 5. Titanium Carbide Thin Film Preparation and Characterisation	 98
5.1 Introduction	98
5.2 Importance of surface quality	100
5.2.1 Surface damage due to polishing	100
5.2.2 Surface roughness	101
5.2.3 Impurities in the form of surface films	102
5.3 Film preparation	103
5.3.1 RF magnetron sputtering	103
5.3.2 Experimental procedure	104
5.4 Film characterisation	106
5.4.1 Film thickness	106
5.4.2 X-Ray reflectometry (XRR)	110
5.4.3 Glancing incidence X-ray diffraction (GIXRD)	117
5.4.4 X-ray photoelectron spectroscopy (XPS)	120
5.5 Concluding remarks	127

6. Elastic Properties of Titanium Carbide Films	129
6.1 Introduction	129
6.2 Measured SBS spectra for TiC films	131
6.2.1 Fast on slow system (<i>TiC/Si</i>)	132
6.2.2 Slow on fast system (<i>TiC/SiC</i>)	136
6.3 Elastic stiffnesses of TiC films	140
6.4 Discussion	146
6.5 Effect of deposition conditions on the elastic properties of TiC films.....	148
6.5.1 Bias voltage.....	148
6.5.2 RF power	152
 7. Platinum Group Alloys: Rh₃Zr and Rh₃Nb	 154
7.1 Introduction	154
7.2 Sample preparation	157
7.3 Density measurement using XRD	158
7.3.1 Theoretical aspects	158
7.3.2 Results and discussion.....	159
7.4 Room Temperature Elastic Stiffnesses of Rh ₃ Zr and Rh ₃ Nb	161
7.4.1 χ^2 minimization of the observed modes	162
7.4.2 χ^2 minimization of the secular functions	173
7.4.3 Discussion	175
 8. Conclusions and outlook	 178
8.1 Summary of results	178
8.2 Suggestions for future work	181
 9. References	 183
List of publications and conferences presentations	203

List of Figures

2.1	The vector diagrams for the conservation of momentum in (a) Stokes scattering and (b) anti-Stokes scattering	24
2.2	The Bragg condition is satisfied by the incident rays of frequency Ω_i and wavevector $\mathbf{k}_i$ scattered by sound waves of wavelength Λ through an angle of φ	28
2.3	Geometry defined for surface Brillouin scattering. Axis 3 is taken to be pointing outwards i.e. normal to the surface.	31
2.4	Typical SBS spectrum in a high symmetry direction for a bulk sample showing the Rayleigh surface acoustic wave (RSAW) peak, transverse wave (TW) threshold, and the longitudinal wave (LW) threshold	43
2.5	Typical SBS spectrum in an arbitrary crystallographic direction for a bulk sample showing the RSAW peak, pseudo surface acoustic wave (PSAW) peak, slow transverse wave (STW) threshold, fast transverse wave (FTW) threshold, lamb shoulder and the longitudinal wave (LW) threshold.....	44
2.6	Geometry defined for the surface wave problem. The axis x_3 is taken to be pointing into the substrate i.e. normal to the surface.	45
2.7	Typical SBS spectrum for a thin supported film showing the Rayleigh surface acoustic wave (RSAW), Sezawa waves (SW), pseudo Sezawa waves (pSW) and sharp resonances.....	48

3.1	Schematic diagram of the experimental arrangement used for surface Brillouin scattering spectroscopy	51
3.2	Schematic representation of a four-level laser transition scheme	52
3.3	Transitions involved in laser action by the Ar^+ ion.	56
3.4	The frequency distribution of longitudinal modes for a single laser line (<i>After instruction manual for Spectra-Physics Model 2060/2080 Ion Laser</i>).....	58
3.5	Etalon loss minimum tuned to laser gain maximum (<i>After instruction manual for Spectra-Physics Model 2060/2080 Ion Laser</i>)	58
3.6	Backscattering geometry defined for SBS experiments, where P1 is an aperture, M2 is the elliptical mirror, LA1 and LA2 are lenses, M3 and M4 are steering mirrors and P2 is the entrance pinhole to the interferometer.	60
3.7	The reflection of a plane wave in a plane parallel plate, Fabry-Perot etalon.....	63
3.8	Transmission of the interferometer as a function of wavelength	64
3.9	Interferogram of a monochromatic spectral line measured by a tandem interferometer (<i>After Mock et. al., 1987</i>).	67
3.10	The principle of tandem scan (<i>after JRS Scientific Instruments, TFPI operator manual</i>)	67
4.1	(a) Velocity dispersion of the modes vs. $q_{\parallel}d$ for TiC/Ge system. The Brillouin intensities for the same system, calculated by the elastodynamic Green's function using the G_{33} component are shown in (b).	85
4.2	Calculated surface-ripple Brillouin spectrum for a 500 nm ($q_{\parallel}d = 11.5$) TiC layer on germanium.	86

4.3	(a) Velocity dispersion of the modes vs. $q_{ }d$ for <i>TiC/Si</i> system. The Brillouin intensities for the same system, calculated by the elastodynamic Green's function using the G_{33} component are shown in (b)	88
4.4	Calculated surface-ripple Brillouin spectrum for a 500 nm ($q_{ }d = 12$) TiC layer on silicon.	89
4.5	Brillouin intensities calculated by the elasto-dynamic Green's function using the G_{33} component for the <i>TiC/diamond</i> system.....	92
4.6	Calculated surface-ripple Brillouin spectrum for a 500nm ($q_{ }d = 11.5$) TiC layer on diamond.....	93
4.7	Brillouin intensities calculated by the elastodynamic Green's function using the G_{33} component for the <i>TiC/SiC</i> system	94
4.8	Calculated surface-ripple Brillouin spectrum for a 500 nm ($q_{ }d = 11.5$) TiC layer on SiC	95
5.1	Rayleigh frequency shift due to surface roughness as a function of $\tau q_{ }$ (<i>After Eguiluz and Maradudin, 1983</i>)	102
5.2	Schematic diagram of RF sputter system with the sputtering process shown adjacent thereto (<i>after www.phasis.ch</i>)	104
5.3	RF magnetron sputtering equipment and the related instruments.....	105
5.4	A sample of TiC thin film on silicon substrate after immersion in alcohol, showing clearly the two step edges.	108
5.5	Profilometer measurement for a film prepared at 200 W showing a layer thickness measurement of about 736 nm.....	108

5.6	Graph of layer thickness against power.....	109
5.7	Interface roughness according Névot and Croce, 1980. The roughness of the interface is described using the Gaussian function (<i>after Filies et al., 1999</i>).....	113
5.8	XRR measurement for a TiC film on silicon prepared at 100 W for 28 min	115
5.9	XRR measurement for a TiC film on silicon prepared at 200 W for 14 min	116
5.10	Schematic diagram of the GIXRD geometry.	118
5.11	GIXRD measurements for TiC films prepared at 100 W, 150 W, 200 W and 250 W.....	119
5.12	XPS survey on the unetched surface of a 488 nm TiC film deposited on silicon at 200 W.....	121
5.13	XPS survey spectrum of a 488 nm TiC film deposited on silicon at 200 W. This was obtained after sputter etching for 1 min.....	122
5.14	XPS survey spectrum of a 488 nm TiC film deposited on silicon at 200 W. This was obtained after sputter etching for 2 min.....	123
5.15	Magnified XPS spectra of C 1s, O 1s, Ti 2p and N 1s XPS spectra for a 488 nm TiC film	125
6.1	Measured SBS spectrum for a 500 nm ($q_{ }d = 11.5$) TiC layer on a Si substrate	132

6.2	Typical measured SBS results for scattering intensity as a function of frequency shift for TiC films on silicon substrates.....	134
6.3	Measured velocity dispersion of the modes vs. $q_{ }d$ for the <i>TiC/Si</i> system	135
6.4	Measured SBS spectrum for a 500 nm ($q_{ }d = 11.5$) TiC layer on a SiC substrate.....	136
6.5	Typical measured SBS results for scattering intensity as a function of frequency shift for TiC films on a silicon carbide substrate.....	138
6.6	Measured velocity dispersion of the modes vs. $q_{ }d$ for the <i>TiC/SiC</i> system	139
6.7	Velocity dispersion curves for (a) <i>TiC/Si</i> and (b) <i>TiC/SiC</i>	141
6.8	Brillouin intensities compared to the measured results for the <i>TiC/Si</i> system.	143
6.9	Brillouin intensities compared to the measured results for the <i>TiC/SiC</i> system.	144
6.10	Calculated and measured SBS spectra for a 500 nm TiC film on a (a) silicon and (b) silicon carbide substrate.....	145
6.11	Velocity dispersion curves of TiC films deposited on silicon substrates under different substrate bias.	150
6.12	Brillouin intensities compared to the measured results for a 550 nm TiC film on a silicon substrate, prepared at a substrate bias of -70V.....	151

6.13	Measured SBS spectra for scattering intensity as a function of frequency shift for TiC films (of layer thickness 350 nm) on a silicon substrate prepared at different RF powers	153
7.1	XRD measurements for (a) Rh ₃ Zr and (b) Rh ₃ Nb.	160
7.2	Angular dependence of the SAW velocities on the (001) surface of Rh ₃ Zr.	164
7.3	The directional dependence of the RSAW, p-SAW and LW velocities on (100) surface of Rh ₃ Zr.	165
7.4	Three dimensional plot of the variation of the χ^2 values with elastic stiffnesses, C_{11} and C_{44} for Rh ₃ Zr.	166
7.5	SBS spectra compared to calculated spectra for different directions (as indicated on each spectrum) from the [100] surface wave direction on the (001) plane surface of Rh ₃ Zr.	168
7.6	Angular dependence of the SAW velocities on the (001) surface of Rh ₃ Nb.	169
7.7	The directional dependence of the RSAW, p-SAW and LW velocities on (100) surface of Rh ₃ Nb.....	170
7.8	Three dimension plot of the variation of the χ^2 values with elastic stiffnesses, C_{11} and C_{44} for Rh ₃ Nb.....	171
7.9	SBS spectra compared to calculated spectra for [100] and [110] surface wave directions ($\alpha = 0^0$ for the [100] direction in (a) and $\alpha = 45^0$ for the [110] direction in (b)) on the (001) plane surface of Rh ₃ Nb.	172

List of Tables

1.1	Independent elastic stiffnesses for different material symmetries	7
5.1	Power vs layer thickness measurements for TiC layer on silicon system.	109
5.2	Deposition rates at different powers for TiC films.	110
5.3	XRR results for TiC films prepared at 100 W, 200 W and 250 W.	117
5.4	Deconvolution of C 1s, O 1s, Ti 2p and N 1s peaks (Moulder, 1995) for the 488nm TiC film	126
6.1	Corresponding $q_{ }d$ values for film thicknesses d for <i>TiC/Si</i>	133
6.2	Corresponding $q_{ }d$ values for film thicknesses d for <i>TiC/SiC</i>	137
6.3	Room temperature elastic stiffnesses of TiC films	146
6.4	Comparison of elastic stiffnesses of TiC films obtained from a 0 V and -70 V substrate bias..	150
7.1	Elastic stiffnesses for Rh ₃ Zr using two different methods	175
7.2	Elastic stiffnesses for Rh ₃ Nb using two different methods	175
7.3	Comparison of experimental and calculated elastic stiffnesses for Rh ₃ Zr.	177
7.4	Comparison of experimental and calculated elastic stiffnesses for Rh ₃ Nb	177
7.5	Elastic stiffnesses for Rh ₃ Zr and Rh ₃ Nb compared to Ni ₃ Al	177

Chapter 1

Introduction

1.1 Background

Modern studies of materials call for knowledge of their elastic properties. Of interest in this study are the elastic stiffnesses which provide information concerning the fundamental interactions occurring in solids, thus enabling interatomic potentials to be developed for the computational modelling of materials with superior qualities. Elastic stiffnesses are related to the engineering moduli used to describe their bulk mechanical properties. Studying these properties therefore leads to information that is of practical value to both the physicist and the engineer.

Surface Brillouin scattering (SBS) is one of several techniques that can be used to determine elastic stiffnesses, as will be discussed in Section 1.3. It provides a wealth of information about elastic properties of bulk solids, thin films, interfaces, and layered materials. The technique has been used here to study both bulk and thin film samples, with the objective of obtaining information on the room temperature

elastic properties of the near-surface region, extending down to a depth of the order of a micron.

Near surface elastic properties are sensitive indicators of residual stress and often differ noticeably from those of the underlying bulk material. There are a number of reasons why this may be the case. It can be due to the presence of a protective coating, near-surface damage caused by polishing, surface heat treatment, or corrosion/oxidation. A high quality surface is therefore of utmost importance for these studies and so techniques such as X-ray reflectometry (XRR), glancing incidence X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) are routinely used to assess surface quality in the present work.

In this Chapter the basic principles of elasticity are given in Section 1.2. Overviews of the primary experimental technique (surface Brillouin scattering) used in the present work and other equivalent techniques currently used to study the elastic properties of materials are given in Section 1.3. Brief introductions of the thin films and bulk materials studied in this work are given in Sections 1.4 and 1.5, respectively. The chapter concludes by giving an outline of the thesis in Section 1.6.

1.2 Elasticity

Solid bodies invariably distort under the influence of applied forces. The deformations may be of any magnitude but in this study we shall restrict our attention to cases where the displacements are small in comparison with the characteristic length dimensions of the body. The theory of elasticity can be

simplified further by considering perfectly elastic bodies i.e., bodies that resume their original shape completely when the forces are relaxed. The force which is exerted on the body per unit area is known as stress. A body is said to be in a stress-free state if all parts of the body are in mechanical equilibrium. When deformation occurs internal forces are produced between the different parts of the body, and the body ceases to be in a state of equilibrium. This effect is referred to as strain. The stress-strain relationship is discussed below followed by an introduction to the basic concepts of elasticity theory of solids. The discussion here is based mainly on the treatments of Nye (1969), Saada (1974) and Musgrave (2003).

1.2.1 Stress and strain

Consider a solid of volume V and surface area S which is in a deformed state. The net force on the body is equal to the sum of all forces on all the volume elements dV and can be written as the volume integral $\int_V F_i dV$, where F_i is the force per unit volume. The volume forces can be expressed as surface forces with the aid of Gauss's divergence theorem

$$\int_V F_i dV = \int_S \sigma_{ij} dA, \quad (1.01)$$

where σ_{ij} is the stress tensor and dA is an element of surface area. F_i is therefore given by

$$F_i = \frac{\partial \sigma_{ij}}{\partial x_j}. \quad (1.02)$$

Nye, (1969) showed that for both homogenous and inhomogeneous stress, the tensor is symmetric

$$\sigma_{ij} = \sigma_{ji}, \quad (1.03)$$

provided that there are no body torques.

In deforming a body, work is done, and for an ideal elastic body this is stored as strain energy. When we consider very small displacements of a three dimensional elastic continuum, the infinitesimal strain tensor η_{ij} is given by

$$\eta_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (1.04)$$

where $\mathbf{u}(x)$ is the particle displacement field referred to the original particle Cartesian coordinates in the unstressed state.

1.2.2 Hooke's law

It has been observed that for sufficiently small stresses the amount of strain is directly proportional to the applied stress (Saada, 1974). This led to the generalised form of Hooke's law which states that, for a perfectly elastic body, each of the components of the state of stress at a point is a linear function of the components of the state of strain at that point. This can be expressed mathematically as

$$\sigma_{ij} = c_{ijkl} \eta_{kl}, \quad (1.05)$$

where c_{ijkl} is a fourth rank tensor, called the elastic constant tensor or the stiffness tensor, with $3^4 = 81$ coefficients. The constants are a measure of the resistance to elastic deformation. Inversely, equation (1.05) can be written as

$$\eta_{ij} = s_{ijkl} \sigma_{kl}, \quad (1.06)$$

where s_{ijkl} is a fourth rank tensor called the elastic compliance, also with 81 coefficients. The compliances are a measure of the ease of deformation.

Since the stress tensor (Eq. 1.03) and the strain tensor (1.04) are symmetric (Saada, 1974), the elastic stiffnesses c_{ijkl} are also symmetric,

$$c_{ijkl} = c_{klij}. \quad (1.07)$$

The symmetry of the c_{ijkl} in the first two and the last two suffixes makes it possible to use the Voigt contracted matrix notation (Nye, 1969) in which the suffixes are abbreviated into a single one running from 1 to 6, such that the elastic stiffnesses can be written as

$$C_{\alpha\beta}, \quad ij \rightarrow \alpha \text{ and } kl \rightarrow \beta \quad (i, j, k, l = 1, 2, 3, \dots; \alpha, \beta = 1, 2, \dots, 6)$$

This leads to the following scheme

Tensor notation:	11	22	33	23,32	31,13	12,21
Matrix notation:	1	2	3	4	5	6

Both the stress and the strain are written with a single suffix running from 1 to 6:

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{31} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{23} & \sigma_{33} \end{bmatrix} \longrightarrow \begin{bmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{bmatrix},$$

$$\begin{bmatrix} \eta_{11} & \eta_{12} & \eta_{13} \\ \eta_{12} & \eta_{22} & \eta_{23} \\ \eta_{13} & \eta_{23} & \eta_{33} \end{bmatrix} \longrightarrow \begin{bmatrix} \eta_1 & \frac{1}{2}\eta_6 & \frac{1}{2}\eta_5 \\ \frac{1}{2}\eta_6 & \eta_2 & \frac{1}{2}\eta_4 \\ \frac{1}{2}\eta_5 & \frac{1}{2}\eta_4 & \eta_3 \end{bmatrix}.$$

Equation (1.05) can now be written as

$$\sigma_\alpha = C_{\alpha\beta} \eta_\beta \quad (\alpha, \beta = 1.2...6) \quad (1.08)$$

The number of independent elastic stiffnesses is therefore significantly reduced as the degree of symmetry increases.

A number of workers (Landau & Lifshitz, 1970; Nye, 1969; Saada, 1974) give detailed derivations of the number of independent stiffnesses for the different crystal systems. For example, there are only two independent elastic stiffnesses for isotropic solids. The form of the elastic stiffness matrix and the numbers of independent constants for different material symmetries, including the isotropic case, are given in Table 1.1. The last two are relevant to the materials studied in this work.

Table 1.1: Independent elastic stiffnesses for different material symmetries.

$$\hat{C} \equiv \frac{1}{2}(C_{11} - C_{12})$$

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix}$$

Triclinic 21

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{bmatrix}$$

Monoclinic 13

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$$

Orthorhombic 9

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \hat{C} \end{bmatrix}$$

Hexagonal 5

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$$

Cubic 3

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \hat{C} & 0 & 0 \\ 0 & 0 & 0 & 0 & \hat{C} & 0 \\ 0 & 0 & 0 & 0 & 0 & \hat{C} \end{bmatrix}$$

Isotropic 2

1.2.3 Engineering moduli

Elastic stiffnesses are related to the engineering moduli used to describe bulk mechanical properties of solids. The engineering moduli can be calculated for both isotropic and anisotropic solids, as described below.

Isotropic Solids

An isotropic solid is one for which the measured stiffnesses are independent of the coordinate system. The pair of constants λ and μ frequently referred to as Lamé constants, after Gabriel Lamé (1795-1870), are defined in terms of elastic stiffnesses:

$$\lambda = C_{12}, \quad \mu = C_{44}, \quad \text{and} \quad \lambda + 2\mu = C_{11}. \quad (1.09)$$

The Poisson's ratio, ν , bulk modulus, K , Young's modulus, E , and the shear modulus, G , are related to these Lamé constants in the following way (Every, 2001):

$$\nu = \frac{\lambda}{2(\lambda + \mu)}, \quad (1.10)$$

$$K = \frac{E}{3(1 - 2\nu)}, \quad (1.11)$$

$$G = \mu. \quad (1.12)$$

Anisotropic Solids

An anisotropic solid is one for which the measured stiffnesses are dependent on the coordinate system, for example an orthotropic material. Orthotropic symmetry is

characterised by two or three mutually orthogonal two-fold axes with rotational symmetry such that its mechanical properties are, in general, different along each of the Cartesian axes. In this case there are three different Young's moduli (Every, 2001), E_α , $\alpha = 1,2,3$, Poisson's ratios $\nu_{\alpha\beta}$, $\alpha,\beta = 1,2,3$, $\alpha \neq \beta$ and shear moduli, $G_{\gamma\gamma}$, $\gamma = 4,5,6$, given by (no summation implied)

$$E_\alpha = \frac{1}{S_{\alpha\alpha}}, \quad \nu_{\alpha\beta} = -E_\beta S_{\alpha\beta}, \quad G_{\gamma\gamma} = \frac{1}{S_{\gamma\gamma}}. \quad (1.13)$$

Young's moduli, Poisson's ratios and shear moduli can also be calculated for other symmetries (Nayfeh, 1995).

1.3 Techniques for studies of elastic properties

Experimental techniques for studies of elastic properties include among others Brillouin scattering and surface Brillouin scattering, ultrasonic methods, inelastic neutron scattering and X-ray scattering, resonance methods and scanning acoustic microscopy. These are now briefly discussed.

1.3.1 Brillouin scattering and surface Brillouin Scattering

Brillouin scattering (BS) is a technique that relies upon the inelastic scattering of photons by thermally activated elastic waves in solids. It is used experimentally to determine the elastic stiffnesses of both liquids and solids. The subject of Brillouin scattering was investigated initially by Brillouin (1922) and Mandelshtam (1926), and ever since it has received considerable attention for characterising elastic and

optoelastic bulk properties of transparent single crystals. The technique has the following advantages:

- it is a non-contact measurement technique;
- the incident and scattered fields leave the sample in thermal equilibrium;
- measurements can be made on very small samples, e.g. $3 \times 3 \times 1 \text{ mm}^3$, and
- measurements can be made on reactive samples provided they are sealed in a protective atmosphere (Catlow *et al.*, 1978; Ngoepe, 1989).

Because of this, BS has been used for studies of elastic properties of transparent materials at high temperatures (Comins *et al.*, 1990; Zouboulis and Grimsditch, 1991) and at high pressures (Zha *et al.*, 1994; Crowhurst *et al.*, 1999).

In the past (pre-1971), one drawback for BS was that it was restricted to the study of bulk modes of transparent materials only, because of poor signal-to-noise ratios. However, development of the tandem Fabry-Pérot interferometer (TFPI) brought about substantial improvements in contrast and has significantly reduced the data collection time required to achieve a good signal-to-noise ratio (Sandercock, 1971; Sandercock, 1980). This has benefited the experimental observation of SBS and has made studies of elastic properties of opaque materials possible.

It is usual to make a distinction between BS and SBS. BS usually refers to light scattering by bulk elastic waves from which the elastic properties of near transparent materials can be determined. SBS on the other hand, involves the study of surface acoustic waves and is important for the determination of elastic properties of opaque and near opaque materials. In opaque materials the high optical absorption restricts

the penetration depth of the laser to a small volume close to the surface. Therefore scattering occurs at or near the surface. The small penetration depth makes the scattering sensitive to the dynamic response of up to a few hundred atomic layers from the surface. As a result SBS is widely used to study the physical properties of thin films (Hillebrands *et al.*, 1985; Grimsditch *et al.*, 1987; Pang *et al.*, 1999; Wittkoski *et al.*, 2004), interfaces (Jorna *et al.*, 1989) and layered materials (Zanoni *et al.*, 1987). In particular it has become useful in the characterization of near surface elastic properties for surfaces affected by ion-implanation, radiation damage, mechanical polishing and other surface modifications (Every, 2002).

In the present work, the SBS technique has primarily been used to provide information concerning the surface acoustic wave speeds in both thin supported films (TiC/Si and TiC/SiC) and bulk materials (Rh₃Zr and Rh₃Nb). In an SBS experiment, the specimen is illuminated with either a 488 nm or 514.5 nm line from an argon-ion laser and the spectrum of the scattered light is examined. The incident laser light is of relatively low power (~hundreds mW). The scattered light is analysed by a Sandercock (3 + 3) multipass TFPI from which the frequency shift of the scattered light with respect to the incident light is determined. The frequency shift together with the scattering geometry gives the phonon velocities from which the elastic stiffnesses are determined.

1.3.2 Ultrasonic methods

Ultrasonic methods are a family of techniques that are widely used for the determination of elastic stiffnesses of anisotropic solids and to study variation of these constants with temperature and pressure. The techniques have been described in a number of books and review articles (Truell *et al.*, 1969; Schreiber *et al.*, 1973; Every and McCurdy, 1992; Every, 1994). In these techniques the stiffnesses are all obtained by measuring the phase velocity of plane acoustic waves propagating along high symmetry directions. The waves are generated and detected by means of piezoelectric transducers. A short burst of high frequency sound (typically 1 MHz to 3 MHz) is generated from the transmitting transducer and propagates through the sample to the receiving transducer. Both pulsed and continuous wave options are used (Bolef and Menes, 1960).

Phase interference or pulse overlap techniques allow high accuracy and sensitivity of better than one part in 10^5 (Williams and Lamb, 1958; McSkimin and Andreatch, 1962; Every, 1994). The high sensitivity makes them suitable for measuring changes in elastic stiffnesses of materials with high accuracy. However the techniques require relatively large samples, careful orientation, cutting and faceting.

1.3.3 Inelastic neutron scattering and X-ray scattering

Inelastic neutron scattering is a well-established method for measuring phonon dispersion relations (Clausen *et al.*, 1985). The phase velocity of phonons can be

obtained for any direction in a single crystal from the slope of the dispersion curve in the long wavelength limit. This allows the elastic stiffnesses of the materials to be determined.

X-ray scattering methods are a family of techniques which reveal information about the crystal structure, chemical composition and physical properties of materials and thin films (Bauwens, 2011). The techniques are based on observing the scattered intensity of an X-ray beam as a function of incident and scattered angle, polarization and energy. The scattering of X-rays is inelastic due to the creation and annihilation of phonons. Therefore, from the measured energy shifts it is possible to obtain the phonon phase velocity and as a result, elastic stiffnesses. This technique has been used successfully to measure elastic moduli in both solids (Miyano *et al.*, 1999) and thin films (Asada *et al.*, 1993).

1.3.4 Resonance methods

These are also a family of techniques commonly used to study elastic properties of both isotropic and anisotropic materials (Xiang and Brill, 1987; Xiang *et al.*, 1989). The techniques have been used to determine elastic stiffnesses of specimens of different shapes including rods, cubes, rectangular parallelepipeds and plates. For specimens in the form of thin wires or fibres, the elastic properties are determined from frequencies of both torsional and flexural vibrations. For specimens in the form of solids, the elastic stiffnesses are determined from the resonance frequencies of the specimens. Resonance frequency is determined by sweeping the frequency on

a suspended specimen. The specimen is suspended between transmitter and receiver transducers, through buffer rods.

1.3.5 Scanning acoustic microscopy (SAM)

SAM, which probes greater depths than surface Brillouin scattering (Section 1.3.1), is an important method for determining elastic stiffnesses of materials (Briggs, 1985). This method has been used to study the elastic properties of a nickel single crystal (Mendik *et al.*, 1992). In SAM sound is directed from a transducer at a small point on a target object. Sound hitting the object is scattered, absorbed, reflected or transmitted. This yields images that are comparable in resolution to images obtained with conventional light microscopes. The contrast in the image arises from the different elastic properties of the microscopic components. The resolution of the image is limited by the physical scanning and the sound beam width. This method is not only limited to the study of elastic properties of materials, it has been used to examine biological specimens, polycrystalline metal surfaces and micro-electronic circuits as well.

1.4 Thin supported films (TiC films)

Group IVB transition metal carbides and nitrides including among others titanium carbide (TiC) and titanium nitride (TiN) are widely used as protective coatings in industrial machining. In particular TiC coatings have excellent properties, such as

high thermal and chemical stability, high thermal conductivity, high hardness and strength and good corrosion resistance. The micro-hardness of TiC, for example, is about 26-31 GPa, which is greater than typical micro-hardnesses of nitrides and carbides of group IVB elements namely: TiN, 20 GPa; ZrN, 16 GPa; ZrC, 21-23 GPa; and HfC, 26 GPa (Kusano *et al.*, 1999).

Several methods are commonly used to prepare TiC films. These include chemical vapour deposition (CVD) (Asada *et al.*, 1993; Konyashin, 1996), pulsed laser deposition (PLD) (Tang *et al.*, 1997; Santerre *et al.*, 1999) and physical vapour deposition (PVD) (Kusano, *et al.*, 1999). Generally, the properties of deposited TiC films depend strongly on the deposition method and conditions. For example, the X-ray Young's modulus of 513 GPa for TiC films prepared by CVD (Asada, 1993) is significantly different to 460 GPa obtained from films prepared by the PVD method (Török *et al.*, 1987). Variations of up to 10% due to different deposition methods are therefore common.

In the present work the PVD method, namely sputtering, was used as it allows the deposition of thin films with the same composition as the target source. The films were then characterized by X-ray reflectometry (XRR), glancing incidence X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) to assess their quality for SBS studies.

Extensive studies on the structure, morphology, chemical composition and mechanical properties of TiC films have been done in the past (Asada *et al.*, 1993; Santerre *et al.*, 1999; Mani *et al.*, 2005; Russias *et al.*, 2005; Yang *et al.*, 2009). The

present work will also make a significant contribution by providing information on the elastic properties.

In practice, film thickness is one of the most important parameters in film coatings as it affects the acoustic behaviour of and internal stress in the films directly. Film thickness generally identifies a specific length scale, since the phonon velocity depends on the ratio of the acoustic length to the layer thickness. Therefore it is necessary to study the dependence of elastic properties as a function of layer thicknesses. This can be done through the SBS measurements of the velocity dispersion of the modes as a function of $q_{||}d$, where $q_{||}$ is the phonon wavevector component parallel to the surface and d is the layer thickness. $q_{||}$ is determined from the scattering geometry.

The observed excitations depend mainly on the over-layer and substrate combination. Thin supported films can be produced such that one has a slow on fast system where the transverse bulk wave velocity in the layer is smaller than that in the substrate. Conversely one can have a fast on slow system. In the former case, the range of acoustic excitations is much richer, with Sezawa waves being observed in addition to the Rayleigh wave. However in the case of a fast on slow system, the measurable excitations are few, making it much more difficult to extract the elastic constants. Further classifications into strong and weak fast on slow or slow on fast systems are possible, depending on the relative shear wave velocities of film and substrate. Simulated velocity dispersion curves are used in the present work to illustrate the differences.

SBS measurements were carried out on two systems, *TiC/Si* and *TiC/SiC*, which were initially categorised as weak fast on slow and weak slow on fast systems. This arose from the use of Voigt-Reuss-Hill averaged elastic constants of the films determined from the values of single crystal TiC.

This assignment was later revised to strong slow on fast system for the *TiC/SiC* after taking into consideration the measured elastic stiffnesses using SBS.

The effects of two deposition conditions, bias voltage and RF power, on the properties of the films have also been studied using SBS.

1.5 Bulk materials (platinum group alloys)

Platinum metal group alloys are promising candidates for future ultra high temperature (≈ 1500 °C) gas turbine materials due to their excellent high-temperature properties. Currently nickel-based superalloys are predominant in high performance applications such as turbine blades in jet aircraft engines and also for gas turbines in power generators. They have extremely high strength at high temperatures because of the $L1_2$ -ordered particles (called γ') coherently embedded in a face-centred cubic (fcc) matrix (called γ) (Wenderoth *et al.*, 2006).

It has been proposed that if the fcc and $L1_2$ coherent two phase structure is formed in an alloy with a higher melting temperature than that of Ni, the alloy would be yet stronger (Yamabe *et al.*, 1996; Yamabe-Mitarai *et al.*, 1997). Because of their exceptional qualities, platinum group metals make good candidates for the base metal in the alloy. Of the six platinum group metals (ruthenium, rhodium palladium,

osmium, iridium and platinum) only the rhodium (Rh) and iridium (Ir) fcc structure can be equilibrated with the $L1_2$ structure. Rh-based rather than Ir-based alloys were chosen for the present work due to their better oxidation resistance, lower thermal expansion coefficient, higher thermal conductivity and lower density (Chen *et al.*, 2004).

In the work presented here, room temperature elastic properties of single crystals of Rh_3Zr and Rh_3Nb are investigated by the surface Brillouin scattering technique. To the best of our knowledge no experimentally measured elastic stiffnesses for Rh_3Zr and Rh_3Nb are available in the literature. However, theoretical calculations using *ab initio* density functional theory (DFT) were reported by Chen *et al.* (2004).

1.6 Outline of the present work

Theoretical aspects of BS and SBS in both transparent and opaque materials are presented in Chapter 2. In that chapter, a description is given of the elasto-optic and the surface ripple scattering mechanisms which are responsible for Brillouin scattering from transparent and opaque materials, respectively. This is followed by a discussion of the elastodynamic Green's function method which invokes only the surface ripple mechanism for the inelastic scattering of light. The Green's function method is used to obtain a calculated Brillouin spectrum for scattering from surface acoustic excitations, for comparison with the measured spectrum.

Chapter 3 focuses on the experimental arrangement of SBS. The underlying principle of a laser and the multipass tandem Fabry-Pérot interferometer (TFPI) are

discussed. Auxiliary optics necessary for the backscattering geometry used in SBS are also described.

Chapter 4 presents calculated results for a supported TiC film based on the formalism of Chapter 2. It also includes the theory involved in calculating elastic stiffnesses of thin films using the Voigt-Reuss-Hill averaging methods.

Chapter 5 gives the details of TiC thin film preparation and characterization. SBS measurements made on TiC films on both silicon and silicon carbide substrates are presented in Chapter 6. Elastic stiffnesses of the films are then extracted from the dispersion curves. The chapter concludes with an examination of the effects of deposition conditions on the properties of films.

Chapter 7 reports on SBS measurements made on the platinum group alloys (Rh_3Zr and Rh_3Nb).

Conclusions and outlook are given in Chapter 8. A bibliography of quoted references and lists of publications and conference presentations conclude the thesis.

Chapter 2

Brillouin and Surface Brillouin Scattering

2.1 Introduction

Brillouin light scattering relies upon the inelastic scattering of photons by thermally activated elastic waves (acoustic phonons). The subject of Brillouin scattering was investigated initially by Brillouin (1922) and Mandelshtam (1926), who predicted light scattering from thermally activated elastic waves. In 1930, Gross (1930) gave experimental confirmation of such a prediction in liquids. The theory of Brillouin scattering was further developed by a number of workers using either the quantum mechanical approach (Born and Huang, 1954; Hayes and Loudon, 1978; Marcuse, 1980) or the classical approach (Benedek and Fritsch, 1966; Cummins and Schoen, 1972; Vacher and Boyer, 1972; Blinc and Zeks, 1974; Berne and Pecora, 1976; Dil, 1982).

It is usual to make a distinction between two aspects of this form of inelastic light scattering. Brillouin scattering (BS) usually refers to light scattering by bulk elastic

waves from which the elastic properties of near transparent materials can be determined. Surface Brillouin scattering (SBS) allows the study of surface acoustic waves and has important applications for opaque and near opaque materials in the determination of their elastic properties. BS and SBS have the advantage of being non-contact measurement techniques.

Since the process is microscopic in nature, Brillouin scattering in general should be treated on the basis of quantum field theory. However in situations where resonance and stimulated Brillouin scattering phenomena are not involved, a classical treatment is usually sufficient.

Brillouin spectroscopy was originally limited to transparent materials. It was only after the introduction of the tandem multi-pass interferometer (Sandercock, 1971; Sandercock, 1980) that both experiment and theory was extended to opaque materials. The quantitative theory of Brillouin scattering in opaque materials has been developed by a number of workers (Bortolani *et al.* 1978; Loudon, 1978a,b; Subbaswamy and Maradudin, 1978; Velasco and Garcia-Moliner, 1980a,b; Zhang *et al.*, 1998; Beghi *et al.*, 2004) over the years using a Green's function approach. In this chapter we present the basic theory of Brillouin scattering in both transparent and opaque materials. The Green's function method for opaque materials is also considered.

2.1.1 Scattering mechanisms

Surface acoustic excitations in the GHz frequency range, which are investigated by SBS and BS can scatter light by two distinct mechanisms, the surface ripple and the elasto-optic mechanism. In the surface ripple mechanism the phonon vibrations cause the surface to appear as a moving grating, i.e., a ripple capable by itself of producing diffraction and changing the frequency of the incoming light (Doppler effect) without invoking any modulation of the dielectric constant in the interior of the crystal, whilst in the elasto-optic scattering mechanism the dynamic fluctuations in the strain field bring about fluctuations in the dielectric constant and these in turn translate into fluctuations in the refractive index. These fluctuating inhomogeneities result in inelastic scattering of the light as it passes through the solid.

The optical transparency of the solid is the main determinant of the relative importance of the scattering mechanism. The bulk elasto-optic scattering is normally larger than the surface-ripple scattering mechanism for transparent media and for opaque materials the surface-ripple mechanism is dominant. Subbaswamy & Maradudin (1978) used aluminium to show that the elasto-optic contribution becomes negligible as compared to the surface ripple mechanism when the material is totally opaque. For semi-opaque materials the elasto-optic contribution cannot be ignored, and therefore both scattering mechanisms must be taken into account in analysing the Brillouin spectrum (Bortolani *et al.*, 1983; Marvin *et al.*, 1980).

The work reported here examines opaque materials. In this case the elastodynamic Green's function method, invoking the surface ripple mechanism for

the inelastic scattering of light, is used to calculate the Brillouin spectrum for scattering from the surface acoustic excitations. The elastodynamic Green's function method is discussed in detail in Section 2.4.

2.1.2 Stokes and anti-Stokes bands

Present in the Brillouin spectrum is a relatively intense central peak, a Stokes band and an anti-Stokes band. The central peak is unshifted in frequency and is as a result of static inhomogeneties and surface roughness in the sample. Stokes and anti-Stokes events appear as a result of first order light scattering in solids. First order light scattering is described as the creation and annihilation of phonons of wave vector $\mathbf{q}$ and frequency ω with energy and momentum conservation. In the long-wavelength limit

$$\Omega_s = \Omega_i - \omega, \quad \mathbf{k}_i - \mathbf{k}_s = \mathbf{q}, \quad (2.01)$$

$$\Omega_s = \Omega_i + \omega, \quad \mathbf{k}_s - \mathbf{k}_i = \mathbf{q}. \quad (2.02)$$

Equation (2.01) corresponds to a Stokes event where a photon loses energy to a phonon whereas in Equation (2.02) a photon gains the energy of the phonon, giving rise to the anti-Stokes event. Ω_i and $\mathbf{k}_i$ are the frequency and the wave vector respectively, of the incident light, while Ω_s and $\mathbf{k}_s$ are the corresponding quantities for the scattered light. Figure 2.1 shows the vector diagrams for the conservation of momentum for the Stokes and anti-Stokes events.

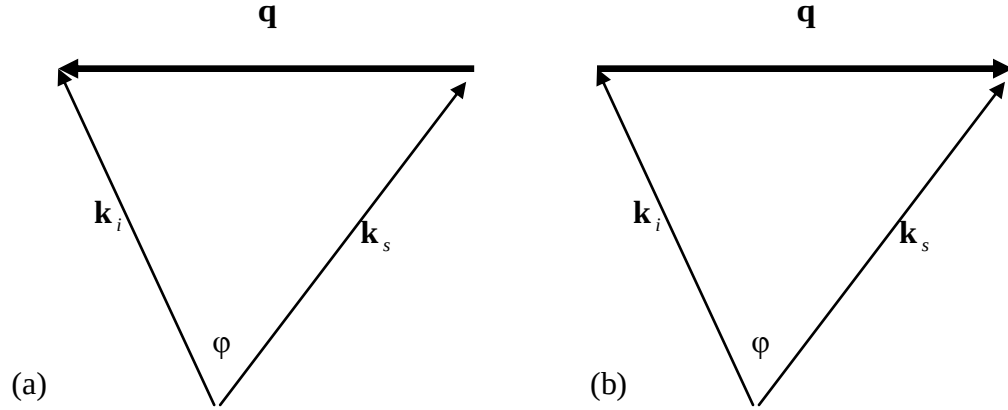


Figure 2.1: The vector diagrams for the conservation of momentum in (a) Stokes scattering and (b) anti-Stokes scattering.

2.2 Brillouin scattering

If a material is not totally opaque or is transparent, the incident light is able to penetrate some distance into the bulk of the material to probe fluctuations in the strain field. Elasto-optic scattering occurs as a result of fluctuations in the dielectric constant caused by the elastic waves moving in thermal equilibrium. The fluctuations cause a change in the refractive index. The change is related to the strain through the elasto-optic constants (Eq. 2.07), which determine the degree of interaction between light and the material.

2.2.1 The Brillouin tensor

Consider a medium with average dielectric constant ε_0 (and refractive index $n = \sqrt{\varepsilon_0}$). Let the incident electric field be a plane wave of the form

$$\mathbf{E}_i(r, t) = \mathbf{n}_i E_0 \exp i(\mathbf{k}_i \cdot \mathbf{r} - \Omega_i t) \quad , \quad (2.03)$$

where $\mathbf{k}_i$ and Ω_i are the incident wave vector and angular frequency, respectively, $\mathbf{n}_i$ is a unit vector in the direction of the incident electric field and E_0 is the field amplitude. The incident electric field produces a polarization in the medium.

When a sound wave of wave vector $\mathbf{q}$ and frequency ω propagates through the medium, the associated compressions and rarefactions (i.e. dynamic fluctuations in the strain field η_{kl}) set up a modulation in the dielectric constant, resulting in inelastic scattering of light passing through the solid. The excess polarization associated with the fluctuations and driven only by the electric field $\mathbf{E}_i$, radiates a scattered field $\mathbf{E}_s$ at a large distance from the scattering region. The scattered field in the far field approximation is given by (Landau and Lifshitz, 1958),

$$\mathbf{E}_s = \frac{\exp(i\mathbf{k}_s \cdot \mathbf{r})}{4\pi\varepsilon_0 r} \mathbf{k}_s \times (\mathbf{k}_s \times \mathbf{G}) \quad , \quad (2.04)$$

where

$$\mathbf{G} = \int_V \delta\varepsilon_{ij} E_j^0 \exp[-i(\mathbf{k}_s - \mathbf{k}_i) \cdot \mathbf{x}] d^3x \quad . \quad (2.05)$$

$\mathbf{E}_s$ is at right angles to direction $\mathbf{k}_s$ of the scattered wave, and is given by the component of the vector $\mathbf{G}$ perpendicular to $\mathbf{k}_s$. $\delta\varepsilon_{ij}$ is the fluctuating part of the susceptibility due to the presence of thermal phonons. In the general anisotropic case of a solid, the dielectric constant ε_{ij} is a tensor of rank 2.

$$\varepsilon_{ij} = \varepsilon \delta_{ij} + \delta\varepsilon_{ij}, \quad (2.06)$$

where ε is the time-independent isotropic susceptibility and δ_{ij} is the Kronecker delta. For small strains the distortion of the dielectric constant tensor $\delta\varepsilon_{ij}$ may be expressed as a linear function of the elastic strain components $\eta_{kl}(\mathbf{x}, t)$

$$\delta\varepsilon_{ij} = -\varepsilon_{ii}\varepsilon_{jj} \sum_{kl} p_{ijkl} \eta_{kl}(\mathbf{x}, t), \quad (2.07)$$

where p_{ijkl} are the Pockels elasto-optic coefficients. The elastic strain components are related to the displacement $\mathbf{u}(\mathbf{x}, t)$ by (Nye, 1969)

$$\eta_{kl}(\mathbf{x}, t) = \frac{1}{2} \left(\frac{\partial u_l}{\partial x_k} + \frac{\partial u_k}{\partial x_l} \right), \quad (2.08)$$

and if we take the Fourier transform of this equation we obtain the strain components in terms of the wave vector $\mathbf{q}$ rather than $\mathbf{x}$

$$\eta_{kl}(\mathbf{q}, t) = \frac{1}{2} [\hat{U}_k(\mathbf{q}, t) \hat{q}_l + \hat{U}_l(\mathbf{q}, t) \hat{q}_k], \quad (2.09)$$

where $\hat{q}_l$ is the unit propagation vector and $\hat{U}_l$ is the unit polarization vector. Taking also the Fourier transform of Eq. (2.07) and substituting Eq. (2.09) into it, we obtain

$$\delta\varepsilon_{ij}(\mathbf{q}, t) = \varepsilon_{ii}\varepsilon_{jj} \frac{1}{2} \sum_{kl} p_{ijkl} [\hat{U}_k \hat{q}_l + \hat{U}_l \hat{q}_k] q\mu(\mathbf{q}, t). \quad (2.10)$$

If we take into consideration that three sound waves with corresponding three possible polarizations propagate with wave vector $\mathbf{q}$, Eq. (2.10) can be written as

$$\delta\varepsilon_{ij}^n(\mathbf{q}, t) = \varepsilon_{ii}\varepsilon_{jj} \frac{1}{2} \sum_{kl} p_{ijkl} [\hat{U}_k^n \hat{q}_l + \hat{U}_l^n \hat{q}_k] q\mu^n(\mathbf{q}, t), \quad (2.11)$$

where μ^n is the amplitude of displacements of atoms from their equilibrium positions, $\hat{U}_k^n$ is the unit polarization vector of the sound wave for the n^{th} mode and q is the corresponding amplitude. Furthermore Eq. (2.11) can be presented in tensor form

$$\delta\epsilon_{ij}^n(\mathbf{q}, t) = q\mu^n \bar{T}_{ij}^n, \quad (2.12)$$

Where $\bar{T}_{ij}^n$ is the Brillouin tensor and its elements are given by

$$\bar{T}_{ij}^n = \frac{1}{2} \epsilon_{ii} \epsilon_{jj} \sum_{kl} [\hat{U}_k^n \hat{q}_l + \hat{U}_l^n \hat{q}_k] p_{ijkl}. \quad (2.13)$$

The Brillouin tensor can be calculated for any given crystal structure and phonon propagation direction (see Landau and Lifshitz, 1958 for examples).

2.2.2 Brillouin scattering in transparent solids

The scattering volume in transparent materials differs from that in opaque materials. In transparent solids most of the scattered light comes from the refracted beam in a region well away from the surface. In opaque and in semi-opaque materials the scattering volume is the surface and the small region near the surface that the light is able to penetrate.

Brillouin light scattering in transparent materials can be viewed as the Bragg reflection of the incident light wave by the diffraction grating created by the thermal phonons. Light scattered from the sound wave fronts must satisfy the Bragg condition (Fig. 2.2), that the path difference between two constructive interfering waves must be an integral multiple of a half wavelength of the incident light. Hence

$$2n\Lambda \sin\left(\frac{\varphi}{2}\right) = \lambda_i, \quad (2.14)$$

where n is the refractive index of the medium, Λ is the wavelength of the sound waves, φ is the angle between incident and scattered light and λ_i is the wavelength of the incident beam. Equation (2.14) can be written in terms of wavevectors

$$2nk_i \sin\left(\frac{\varphi}{2}\right) = q. \quad (2.15)$$

For long wavelength phonons with velocity V ,

$$\omega = Vq. \quad (2.16)$$

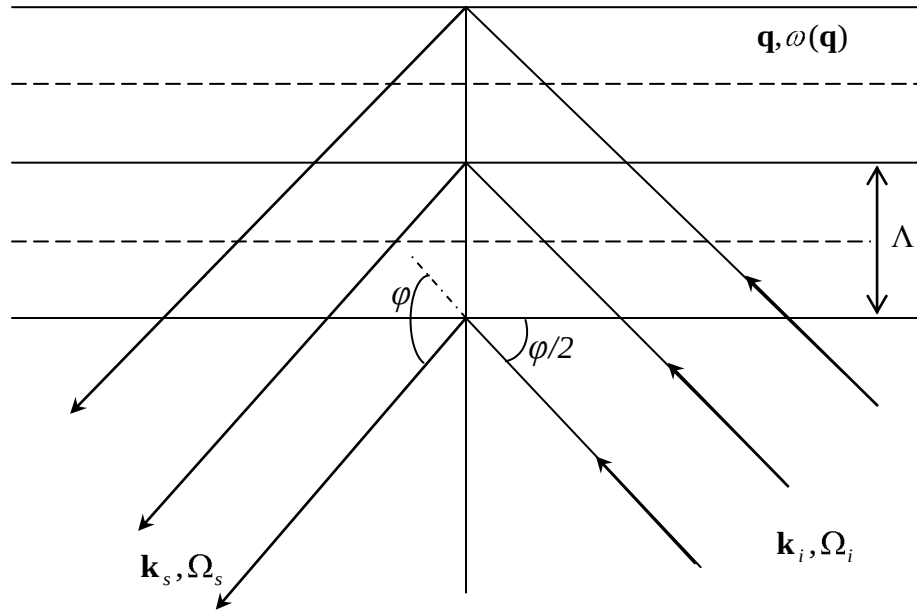


Figure 2.2: The Bragg condition is satisfied by the incident rays of frequency Ω_i and wavevector $\mathbf{k}_i$ scattered by sound waves of wavelength Λ through an angle of φ .

Substituting Eq. (2.16) in (2.15) and using Eq. (2.02) we find that

$$\Delta\Omega_B = \pm \frac{2nV\Omega_i}{c} \sin\left(\frac{\varphi}{2}\right), \quad (2.17)$$

where $\Delta\Omega_B = \Omega_s - \Omega_i$ is called the Brillouin shift and c is the velocity of light. Since $k_i = \Omega_i / c$, the phonon velocity V is given by

$$V = \frac{\Delta\Omega_B}{2nk_i \sin\left(\frac{\varphi}{2}\right)}. \quad (2.18)$$

Nizzoli and Sandercock (1990) obtained the same equation (2.18) by using a quantum mechanical approach, where the Brillouin scattering is considered as scattering of a photon by a phonon. In a backscattering configuration ($\varphi = 180^\circ$), Eq. (2.18) simplifies to

$$V = \frac{\Delta\Omega_B}{2nk_i}. \quad (2.19)$$

Eqs. (2.18 and 2.19) show that in order to measure bulk sound velocities in a transparent medium by Brillouin scattering the refractive index is required. However, work by Krüger *et al.*, (1998) using a special geometry, namely the reflection induced **ΘA** scattering geometry (**RIΘA**) demonstrates that the elastic properties of transparent material can be determined using Brillouin scattering without the refractive index being known.

2.3 Surface Brillouin scattering

2.3.1 Conservation laws

In SBS, the sample surface is usually illuminated with an argon-ion laser of angular frequency Ω_i and wave vector $\mathbf{k}_i$ at an angle θ_i to the normal. Most of this light is either reflected, refracted or absorbed. A small amount of it is diffusely scattered, undergoing in the process a fractional change in frequency. The spectrum of the scattered light is examined by the multipass Tandem Fabry-Perot Interferometer (TFPI). A detailed description of the TFPI is given in Chapter 3.

As discussed in Section 2.1.1, the surface ripple scattering mechanism does not occur in the bulk of the material but at the surface. The phonons present at the surface move in thermal equilibrium, creating a corrugation of the surface which can diffract the incoming light. In opaque materials the high optical absorption restricts the penetration depth to a volume close to the surface, which influences the phonon wave vector conservation rule. The permittivity is generally complex for an opaque material leading to complex wave vector components perpendicular to the surface, which implies that the wave vector conservation is only valid for components parallel to the surface ($\mathbf{q}_{\parallel}$) in opaque materials. Thus Eq. (2.01) and (2.02) becomes

$$\pm(\mathbf{k}_s - \mathbf{k}_i) = \mathbf{q}_{\parallel}. \quad (2.20)$$

2.3.2 Kinematics of surface Brillouin scattering

Figure 2.3 shows a typical geometry for a Brillouin light scattering experiment. Light of wave vector $\mathbf{k}_i$ is scattered by a phonon with wave vector $\mathbf{q}$ parallel to the surface. The surface is in the 1-2 plane and the sagittal plane that contains the incident wave vector $\mathbf{k}_i$ is the 1-3 plane. Angle φ separates the projections of $\mathbf{k}_i$ and $\mathbf{k}_s$ onto the sample surface, such that $\alpha = 180 - \varphi$. α is the azimuthal angle.

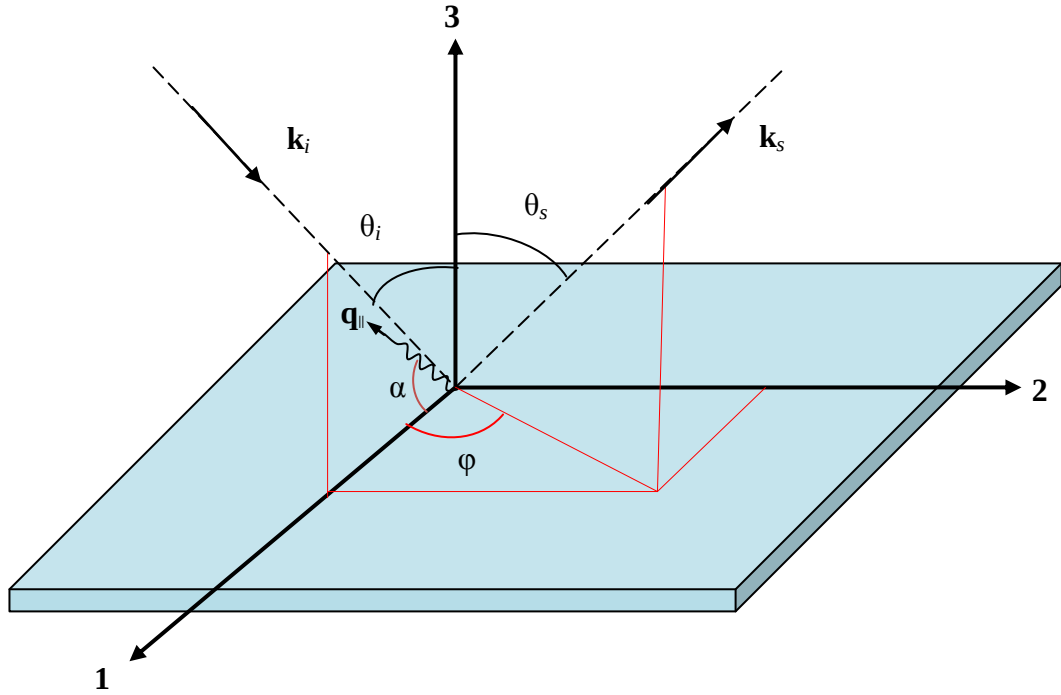


Figure 2.3: Geometry defined for surface Brillouin scattering. Axis 3 is taken to be pointing outwards i.e. normal to the surface.

For the coordinate system shown, the components of $\mathbf{q}_{\parallel}$ are

$$q_1 = k_i \sin \theta_i + k_s \sin \theta_s \cos \varphi, \quad (2.21)$$

$$q_2 = k_s \sin \theta_s \sin \varphi. \quad (2.22)$$

Since the phonon velocity is much smaller than the velocity of light, we take

$k_i = k_s$ and obtain

$$q_{\parallel} = k_i [\sin^2 \theta_i + 2 \sin \theta_i \sin \theta_s \cos \varphi + \sin^2 \theta_s]^{1/2}. \quad (2.23)$$

In a backscattering geometry, it is common to make the approximation $\theta_i = \theta_s$ and

$\varphi = 0$, which reduces Eq. (2.23) to

$$q_{\parallel} = 2k_i \sin \theta_i. \quad (2.24)$$

The phonon velocity is then given by

$$V = \frac{\Delta \Omega_B}{2k_i \sin \theta_i}. \quad (2.25)$$

It is noted that the result expressed in Eq. 2.25 and used in the present SBS experiments to measure the velocity of surface acoustic waves in opaque materials by means of a backscattering geometry is independent of the refractive index of the material.

2.3.3 Scattering cross section for the ripple mechanism

Loudon and Sandercock (1980) showed that the scattering cross section for the ripple mechanism has a complicated dependence on the incident and scattering angles as well as on the polarization of light. It is proportional to the power spectrum of the

normal displacements of the surface wave vector component $\mathbf{q}_{\parallel}$; this in turn is proportional to $(n(\omega)+1)\text{Im } \tilde{G}_{33}(q_{\parallel}, \omega+i0)$. $n(\omega)$ is the phonon occupation number and $\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega+i0)$ is the component of the Fourier domain elastodynamic Green's function pertaining to force and response normal to the surface.

Considering the treatment of Subbaswamy and Maradudin (1978), the scattering efficiency for an incident radiation polarised in either parallel or perpendicular to the plane of incidence is given by

$$\frac{d^2 Z_{\eta}}{d\Omega_s d\omega} = \frac{\omega_0^4 \cos \theta_s}{c^2 \omega_s^2} \frac{\hbar(n(\omega)+1)}{8\pi^3 \rho} \text{Re} \sum_{i,j=1}^2 (A_{ij}^{(n)}(\mathbf{q}_{\parallel}, \omega)). \quad (2.26)$$

For ripple scattering alone

$$A_{22}^{(n)}(\mathbf{q}_{\parallel}, \omega) = iT_{\eta\eta}^{(22)} \mathcal{D}_{33}(\mathbf{q}_{\parallel}, \omega) \quad (2.27)$$

where $T_{\eta\eta}^{22}$ is a function of

$$\mathcal{D}_{33}(\mathbf{q}_{\parallel}, \omega) = \tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega+i0) - \tilde{G}_{33}^*(\mathbf{q}_{\parallel}, \omega+i0) = 2i \text{Im } \tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega+i0),$$

the polarization ($\parallel$ or $\perp$), dielectric constant ϵ_0 , incident angle θ_i and scattered angle θ_s . Substituting Eq. (2.27) into (2.26), the scattering efficiency reduces to

$$\frac{d^2 Z_{\eta}}{d\Omega_s d\omega} = \frac{\omega_0^4 \cos \theta_s}{c^2 \omega_s^2} \frac{\hbar(n(\omega)+1)}{8\pi^3 \rho} \text{Re } iT_{\eta\eta}^{22} \mathcal{D}_{33}(\mathbf{q}_{\parallel}, \omega). \quad (2.28)$$

In the classical limit ($k_B T \gg \hbar \omega$) (a condition that is satisfied for Brillouin scattering at room temperature and above) and making the approximations $n(\omega)+1 \approx k_B T / \hbar \omega$ and $\omega_s \approx \omega_0$, the efficiency is given by

$$\frac{d^2 Z_\eta}{d\Omega_s d\omega} = \frac{D}{\omega} \text{Im} \tilde{G}_{33}(\mathbf{q}_\parallel, \omega + i0) , \quad (2.29)$$

where

$$D = \frac{-\omega_0^2 \cos \theta_s k_B T \text{Re} T_{\eta\eta}^{22}}{4\pi^3 c^2 \rho} , \quad (2.30)$$

is a factor that depends on the scattering geometry, incident photon frequency, temperature and the optical properties of the medium. The equation for the scattering cross section (2.28) does not only apply to Brillouin scattering from the free surface of a semi-infinite solid, but it also applies to scattering from the interface of two perfectly bonded solids which can either be a combination of a transparent and an opaque material or can be a thin supported film. $\tilde{G}_{33}(\mathbf{q}_\parallel, \omega)$ is used to calculate the Brillouin spectrum for scattering from the surface acoustic excitations of highly opaque materials. The quantitative evaluation of $\tilde{G}_{33}$ is outlined in the following section; it follows closely the approach developed by Zhang *et al.*, (1998) and Beghi *et al.*, (2004).

2.4 Elastodynamic Green's function method

We will consider the elastodynamic Green's function responses on both solid and thin film surfaces. In the case of a transparent layer on an opaque substrate the elasto-optic contribution from the layer and the scattering from the film/substrate interface must be taken into account. However this can be ignored in the case of an opaque film supported by either an opaque or transparent substrate. For the thin opaque films e.g. TiN and TiC, light scattering by surface ripple mechanism

dominates that by elasto-optic coupling. It has been shown that (Eq. 2.29), at a given temperature T and frequency ω the SBS scattering efficiency $I(\omega)$ for the surface ripple mechanism is given by

$$I(\omega) = \frac{AT}{\omega} \text{Im}\{\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega)\}. \quad (2.31)$$

A is a factor that depends on the scattering geometry, incident photon frequency, and optical properties of the medium. The response function $\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega)$ represents the x_3 -component of the displacement response of the surface to a periodic force acting on that surface in the x_3 -direction with temporal and spatial frequencies ω and $\mathbf{q}_{\parallel} = (q_1, q_2)$ respectively. The displacement field $\mathbf{u}(\mathbf{x}, t)$, is governed by the wave equation

$$\rho \frac{\partial^2 u_i}{\partial t^2} = c_{ijkl} \frac{\partial^2 u_l}{\partial x_j \partial x_k}, \quad (2.32)$$

where ρ is the density, u_i are the displacement components measured along the Cartesian axes x_i to which the elastic stiffness tensor c_{ijkl} is referred. Summation over repeated subscripts is followed.

2.4.1 Bulk waves

The simplest solutions for equation (2.32) are plane sinusoidal waves given by the real part of

$$\mathbf{u}(\mathbf{x}, t) = \mathbf{U} \exp[iq(l_i x_i - vt)], \quad (2.33)$$

where $\mathbf{U} = \hat{n}_k U_k$, U_k is the polarization factor which represents the amplitude of motion and $\hat{n}_k$ is a unit vector along the x_k axis. The phase velocity v is measured along the propagation vector $\mathbf{q}$, whose direction cosines are given by l_i . Direction cosines l_i , phase velocity v , and the polarization U_k are related by the set of three linear equations

$$(c_{ijkl} l_j l_l - \rho v^2 \delta_{ik}) U_k = 0, \quad (2.34)$$

where δ_{ik} is the Kronecker symbol. Eq. (2.34) is known as the Christoffel equation and is the bulk wave solution for a medium that is infinite in all directions. It is obtained explicitly by substituting the plane wave equation (2.33) into the wave equation (2.32). By introducing the second rank tensor

$$\Gamma_{ik} = c_{ijkl} l_j l_l, \quad (2.35)$$

the Christoffel equation becomes

$$(\Gamma_{ik} - \rho v^2 \delta_{ik}) U_k = 0. \quad (2.36)$$

This shows that the polarization U_k is the eigenvector of the Γ_{ik} tensor with the eigenvalue ρv^2 . For non-trivial solution we require the determinant of the coefficients to be equal to zero, resulting in the secular equation

$$\left| \Gamma_{ik} - \rho v^2 \delta_{ik} \right| = 0, \quad (2.37)$$

which generates a cubic equation in v^2 (Farnell, 1970). For a given propagation direction, there are three velocities, which are the three roots of the secular equation (2.37). The roots are the squares of the velocities for the three bulk waves. Each

velocity is related to an eigenvector which defines the displacement direction (i.e. the wave polarization).

Since the stiffness tensor c_{ijkl} is symmetric, then Γ_{ik} is also symmetric, $\Gamma_{ik} = \Gamma_{ki}$. Therefore its eigenvalues are real and the eigenvectors of the three solutions are orthogonal, one displacement vector being quasi-longitudinal and the other two being quasi-transverse. These waves are purely longitudinal or transverse only for propagation along high symmetric directions, where the eigenvectors are respectively parallel and perpendicular to the propagation vector.

2.4.2 Surface waves

Surface waves are wave packets resulting from appropriate stress and strain boundary conditions, which propagate through, or on the surface of a medium without causing permanent deformation of any point in the medium. One such wave is a Rayleigh wave which propagates at the surface of any semi-infinite medium. Lord Rayleigh (1887) discovered this wave. Rayleigh analysed the propagation of elastic waves on the boundary of an infinite half-space. He found that the displacement amplitude of the propagating Rayleigh waves decays exponentially with depth beneath the surface, with its associated energy density concentrated within a distance of order of a wavelength below the surface. He further observed that particle motion at any point on or below the surface was in an elliptical path perpendicular to the surface, while the energy flow was parallel to the surface.

Solutions for the surface waves are sought which decay with depth below the surface $x_3 = 0$ and which are ‘straight crested’ in that there is no dependence of the displacement on the distance measured perpendicular to the sagittal plane. The propagation vector in the surface is defined by its magnitude q and its direction cosines l_1 and l_2 on x_1 and x_2 axes, respectively. Thus the plane wave solution can be modified such that the solutions of a surface wave are assumed to be a linear combination of terms of the form (Farnell, 1970)

$$u_i = \alpha_i \exp[iql_3x_3] \exp[iq(l_1x_1 + l_2x_2 - vt)], \quad (2.38)$$

which satisfy the wave equation and boundary conditions. One condition for the surface wave problem is that the quantity l_3 in each of the terms of the solutions must vanish as $x_3 \rightarrow -\infty$. The wave like properties of the solution are taken to be contained in the part $\exp[iq(l_1x_1 + l_2x_2 - vt)]$ of equation (2.38), while the x_3 -dependence is regarded as part of the amplitude of the terms. Thus the propagation vector is always assumed to be parallel to the surface even though there may be a real part in l_3 . On substituting equation (2.38) into the wave equation (2.32), the same set of homogeneous equations (2.34) and secular equation (2.37) are obtained as in the case of plane bulk waves in an unbounded medium.

The secular equation for the surface-wave case

$$\left| \Gamma_{jk} - \delta_{jk} \rho v^2 \right| = 0 \quad (2.39)$$

can be regarded as a cubic equation in v^2 with l_3 as a parameter or a sextic equation in l_3 with v as a parameter. Thus for any value of v , the root l_3 , of the equation

(2.39) gives a solution of the form of equation (2.38) satisfying the anisotropic wave equation and representing a wave travelling with a phase velocity v in the direction $i_1 l_1 + i_2 l_2$ and having an x_3 –dependence governed by the value l_3 . Since l_1 and l_2 are assumed to be real, coefficients of the powers of l_3 in the secular equation (2.39) are also real. As a result there are in general, three pairs of complex-conjugate roots to this equation for each value of v (Farnell, 1970).

For an isotropic case, all the roots lie on the imaginary axis of the complex plane. However in an anisotropic medium with propagation in a crystal plane of mirror symmetry or in certain high-symmetry directions, equation (2.39) becomes bicubic and the roots have inversion symmetry in the origin of the complex plane. For general anisotropic conditions, the only restriction is that the complex roots must occur in conjugate pairs.

The roots lying in the upper half of the complex plane correspond to waves of the form of equation (2.38) which become infinite as $x_3 \rightarrow -\infty$. For normal surface-wave problems on infinitely deep substrates these solutions of the wave equation can be ignored because they do not satisfy the boundary condition that the displacements vanish at large depths. As a result only three outgoing waves in the substrate having polarization vectors that correspond to perpendicular wave vectors $q_3^{(n)}$ ($n = 7, 8, 9$) are retained as physical and the three incoming waves are discarded. In the layer all the six partial waves having polarization vectors corresponding to perpendicular wave vectors $q_3^{(n)}$ ($n = 1, 2, 3, 4, 5, 6$) are used.

2.4.3 Green's function for the surface of a bulk solid

The quantitative evaluation of the Green's functions outlined in this and the following sections follows closely the approach developed by Every (1996), Zhang *et al.*, (1998) and Beghi *et al.*, (2004).

We consider an elastically anisotropic half-space of density ρ and elastic stiffness tensor c_{ijkl} occupying the halfspace $x_3 > 0$. It is assumed that a time- and position-dependent point force $\mathbf{F}(\mathbf{x}, t)$ acts at the origin on the otherwise free surface of the halfspace. The body force $\mathbf{F}(\mathbf{x}, t)$ is defined per unit mass and has a harmonic time dependence

$$\mathbf{F}(\mathbf{x}, t) = \mathbf{F}(\mathbf{x}) \exp(-i\omega t). \quad (2.40)$$

The displacement field $\mathbf{u}(\mathbf{x}, t)$ in response to this force is given by

$$u_i(\mathbf{x}, t) = G_{ij}(\mathbf{x}, t) F_j \quad (2.41)$$

where $G_{ij}(\mathbf{x}, t)$ is the elastodynamic Green's tensor. In evaluating the response the boundary conditions on the stress tensor must include the force at the origin as

$$\sigma_{l3}(\mathbf{x}_{\parallel}, x_3 = 0_+, t) = -F_j \delta_{jl} \delta(\mathbf{x}_{\parallel}) \delta(t) \quad (2.42)$$

$\mathbf{x}_{\parallel} = (x_1, x_2)$ denotes the position vector in the surface and $\delta(\mathbf{x}_{\parallel}) = \delta(x_1) \delta(x_2)$ is a two dimensional δ -function. The negative sign in equation (2.42) shows that the surface tractions are reactions to the applied force. The Fourier transform of the surface traction with respect to $\mathbf{x}_{\parallel}$ and t is

$$\sigma_{l3}(\mathbf{x}_{\parallel}, x_3 = 0_+, t) = -\frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 q_{\parallel} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} F_j \delta_{jl} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} - \omega t) . \quad (2.43)$$

As noted above, the displacement field $\mathbf{u}(\mathbf{x}, t)$ is governed by the wave equation, which admits six plane wave solutions for each value of $\mathbf{q}_{\parallel}$ and ω . In this case of the surface of a solid, only 3 outgoing waves are retained as physical. A general solution is taken to be a superposition of these waves with their amplitudes proportional to $\mathbf{F}$;

$$u_i(\mathbf{x}, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{n=1}^3 A_j^{(n)} F_j U_i^{(n)} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} + q_3^{(n)} x_3 - \omega t) . \quad (2.44)$$

Inserting equation (2.44) into the stress-strain relationship $\sigma_{lm} = c_{lmpq} \partial u_p / \partial x_q$ gives the surface tractions as

$$\sigma_{l3}(\mathbf{x}_{\parallel}, x_3 = 0_+, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} i\omega \sum_{n=1}^3 A_j^{(n)} F_j B_l^{(n)} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} - \omega t) , \quad (2.45)$$

where

$$B_l^{(n)} = \sum_{pq} c_{3lpq} U_p^{(n)} q_q^{(n)} / \omega . \quad (2.46)$$

A set of three linear equations

$$\sum_{n=1}^3 B_l^{(n)} A_j^{(n)} = i\delta_{lj} / \omega , \quad (2.47)$$

for the partial wave amplitudes $A_j^{(n)}$ is obtained by comparing equations (2.43) and

(2.45). The solution of the linear equations is $A_j^{(n)} = \frac{i}{\omega} (\mathbf{B}^{-1})_j^{(n)}$, which can also be

written as

$$A_j^{(n)} = \frac{i}{\omega} \frac{\text{adj}(\mathbf{B})_j^{(n)}}{|\mathbf{B}|} . \quad (2.48)$$

By substituting results for $A_j^{(n)}$ into equation (2.44) and then using equation (2.41), we obtain the elastodynamic Green's tensor,

$$G_{ij}(\mathbf{x}, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{i}{\omega} \sum_{n=1}^3 \Lambda_{ij}^{(n)} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} + q_3^{(n)} x_3 - \omega t) , \quad (2.49)$$

where
$$\Lambda_{ij}^{(n)} = (\mathbf{B}^{-1})_j^{(n)} U_i^{(n)} . \quad (2.50)$$

By taking the limit $x_3 \rightarrow 0_+$ and setting $ij = 33$, we obtain the surface Green's function for normal force and normal displacement

$$G_{33}(\mathbf{x}_{\parallel}, x_3 = 0_+, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left\{ \frac{i}{\omega} \sum_{n=1}^3 \Lambda_{33}^{(n)} \right\} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} - \omega t) . \quad (2.51)$$

The normal component of the Fourier domain elastodynamic Green's function that determines the Brillouin spectrum for the surface is given by

$$\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega) = \frac{i}{\omega} \sum_{n=1}^3 \Lambda_{33}^{(n)}(\mathbf{q}_{\parallel}/\omega) , \quad (2.52)$$

and using (2.50) this reduces to

$$\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega) = \sum_{n=1}^3 \frac{i}{\omega} (B^{-1})_3^{(n)} U_3^{(n)} . \quad (2.53)$$

This implies that the Green's function for the surface of a solid is represented by the linear combination of the three outgoing plane waves in the solid having polarization vectors $U_3^{(n)}$ that correspond to the perpendicular wave vector $q_3^{(n)}$, $n = 7, 8, 9$. B is the boundary condition matrix. When the inverse of the boundary value matrix B^{-1} becomes singular, a true surface wave arises (Rayleigh surface acoustic wave) and a sharp line will be visible in the spectrum (Comins *et al.*, 2000). Figure 2.4 shows a typical SBS spectrum in a high-symmetry direction (e.g. [100] or [110])

crystallographic directions) for a bulk sample. The solutions $n = 7,8,9$ in the region before the transverse bulk wave (TW) threshold, $\omega_T = q_{//}v_T$, have complex $q_3^{(n)}$ and all waves are true surface waves. In the region after the longitudinal wave (LW) threshold, $\omega_L = q_{//}v_L$, all modes, transverse and longitudinal, are propagating bulk waves with real $q_3^{(n)}$. Between these limiting frequencies ω_T and ω_L , there are mixed modes with both complex and real values of $q_3^{(n)}$, $n = 7,8,9$.

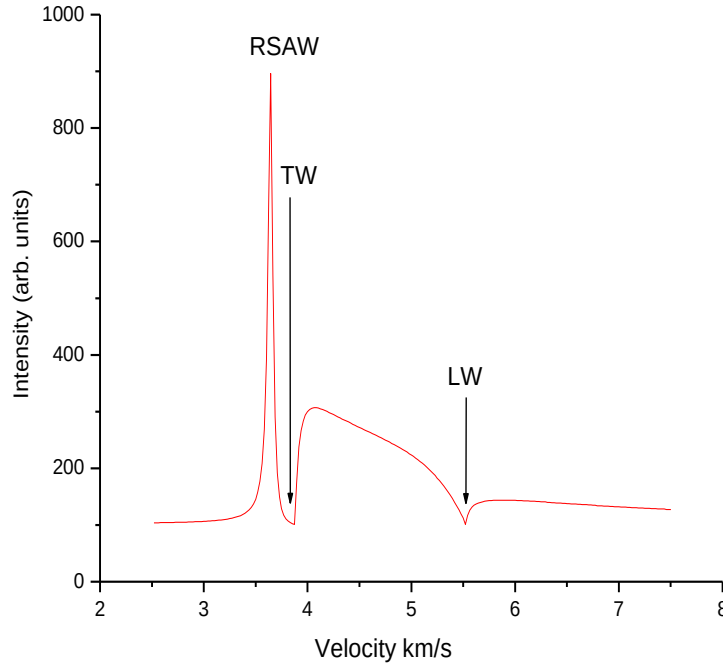


Figure 2.4: Typical SBS spectrum in a high symmetry direction for a bulk sample showing the Rayleigh surface acoustic wave (RSAW) peak, transverse wave (TW) threshold, and the longitudinal wave (LW) threshold. The region starting from the TW threshold and extending over the entire bulk wave continuum is known as the Lamb shoulder.

There may be sharp resonances where B^{-1} is small but non-zero, leading to a pseudo-surface acoustic wave (pSAW) within the region of the Lamb shoulder. This occurs in low-symmetry directions. In these directions, the Green's function calculations predict both the fast transverse wave (FTW) and the slow transverse wave (STW) in addition to the PSAW (Fig. 2.5).

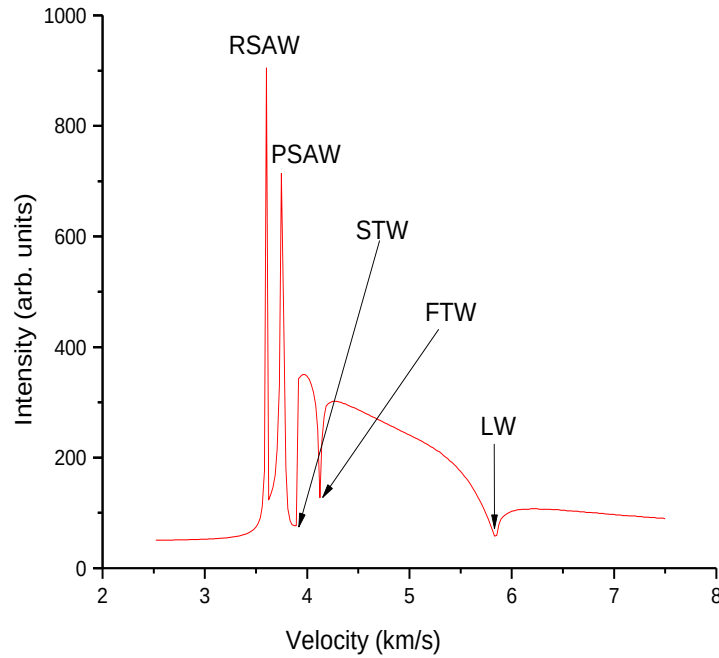


Figure 2.5: Typical SBS spectrum in an arbitrary crystallographic direction for a bulk sample showing the RSAW peak, pseudo surface acoustic wave (PSAW) peak, slow transverse wave (STW) threshold, fast transverse wave (FTW) threshold, lamb shoulder and the longitudinal wave (LW) threshold. The FTW and STW degenerate to the bulk TW in high symmetry directions.

2.4.4 Green's function for the surface of an opaque film

Figure 2.6 shows the chosen coordinate system with x_3 defined as outward normal to the traction free surface of the layer which occupies the half space $x_3 < 0$. The scattering in an opaque layer occurs at the free surface of the layer and requires the evaluation of $\tilde{G}_{33}(q_{\parallel}, x_3 = -d, \omega)$.

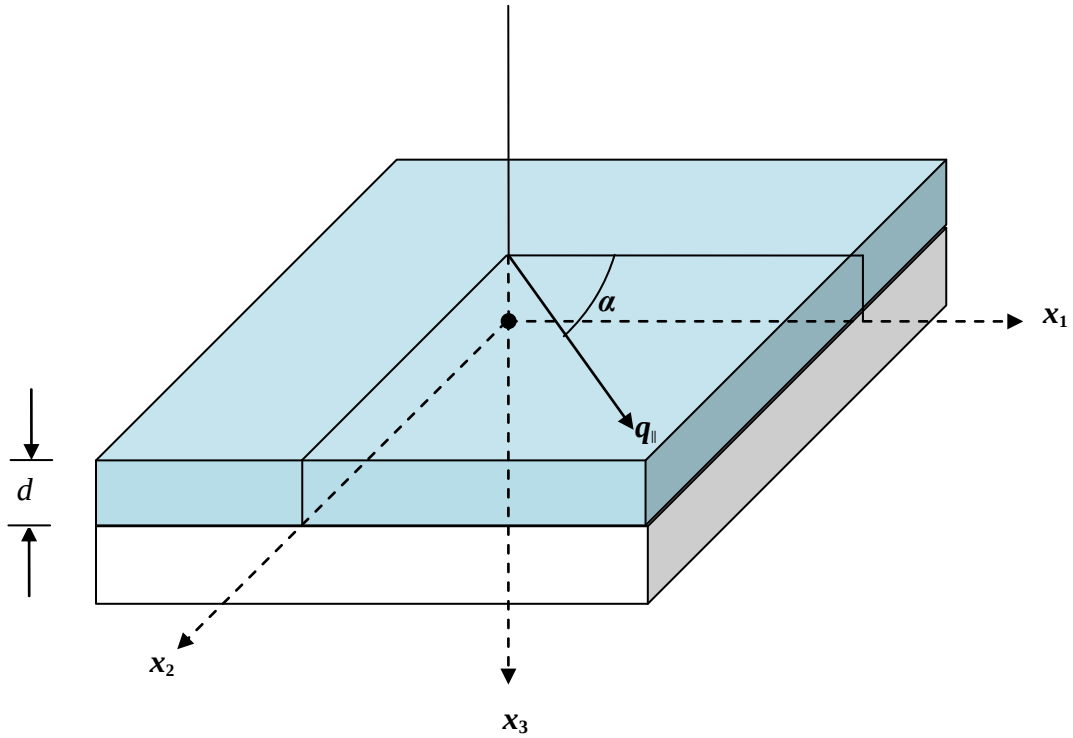


Figure 2.6: Geometry defined for the surface wave problem. The axis x_3 is taken to be pointing into the substrate i.e. normal to the surface.

We consider a supported opaque film with layer thickness d and occupying the half space $x_3 < 0$ (Fig. 2.6). In calculating $\tilde{G}_{33}(q_{\parallel}, x_3 = -d, \omega)$ for thin films we consider, as before, the response to a δ -function force acting on the surface of the film. The boundary conditions to be satisfied are the continuity of stress ($\sigma_{l3}(q_{\parallel}, x_3 = 0, \omega)$; $l = 1, 2, 3$) components and displacement field $\mathbf{u}(\mathbf{x}, t)$ at the interface, and $\sigma_{l3}(q_{\parallel}, x_3 = -d, \omega) = -\delta_{l3}$ at the free surface. The solution that satisfies the boundary conditions in the layer takes the form of a superposition of six plane waves

$$u_i^-(\mathbf{x}, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{n=1}^6 A_j^{(n)} F_j U_i^{(n)} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} + q_3^{(n)} x_3 - \omega t) , \quad (2.54)$$

and three outgoing waves in the substrate

$$u_i^+(\mathbf{x}, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{n=7}^9 A_j^{(n)} F_j U_i^{(n)} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} + q_3^{(n)} x_3 - \omega t) . \quad (2.55)$$

Using stress-strain relationship $\sigma_{lm} = c_{lmpq} \partial u_p / \partial x_q$ and Eq. (2.54) for the layer, we

obtain the surface tractions as

$$\sigma_{l3}^-(\mathbf{x}_{\parallel}, x_3 = -d, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} i\omega \sum_{n=1}^6 A_j^{(n)} F_j B_l^{(n)} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} - \omega t) , \quad (2.56)$$

where

$$B_l^{(n)} = \sum_{pq} C_{3lpq}^- U_p^{(n)} q_q^{(n)} \exp -iq_3^{(n)} d / \omega , \quad n = 1, 2, 3 \dots 6. \quad (2.57)$$

Comparing (2.54) and (2.56) we obtain a set of 3 linear equations for the partial wave amplitudes $A_j^{(n)}$

$$\sum_{n=1}^6 B_l^{(n)} A_j^{(n)} = i\delta_{jl} / \omega , \quad l = 1, 2, 3. \quad (2.58)$$

Taking into consideration the continuity of stress at the interface

$$\sigma_{l3}^+(\mathbf{x}_{\parallel}, x_3 = 0_+, t) - \sigma_{l3}^-(\mathbf{x}_{\parallel}, x_3 = 0_-, t) = 0, \quad (2.59)$$

we obtain another set of three equations for the amplitudes

$$\sum_{n=7}^9 B_l^{(n)} A_j^{(n)} = 0, \quad l = 4, 5, 6 \quad (2.60)$$

where

$$B_l^{(n)} = \sum_{pq} C_{3l-3pq}^+ U_p^{(n)} q_q^{(n)} / \omega \quad l = 4, 5, 6 \quad n = 7, 8, 9 \quad (2.61)$$

and

$$B_l^{(n)} = -\sum_{pq} C_{3l-3pq}^- U_p^{(n)} q_q^{(n)} / \omega \quad l = 4, 5, 6 \quad n = 1, 2, 3 \dots 6. \quad (2.62)$$

From the continuity of the displacement field at the boundary,

$$u_i^+(\mathbf{x}_{\parallel}, x_3 = 0_+, t) - u_i^-(\mathbf{x}_{\parallel}, x_3 = 0_-, t) = 0, \quad (2.63)$$

three equations for the partial wave amplitudes arise

$$\sum_{n=7}^9 B_l^{(n)} A_j^{(n)} = 0, \quad l = 7, 8, 9 \quad (2.64)$$

where

$$B_l^{(n)} = U_{l-6}^{(n)}, \quad l = 7, 8, 9, \quad n = 7, 8, 9, \quad (2.65)$$

and

$$B_l^{(n)} = -U_{l-6}^{(n)}, \quad l = 7, 8, 9, \quad n = 1, 2, 3 \dots 6. \quad (2.66)$$

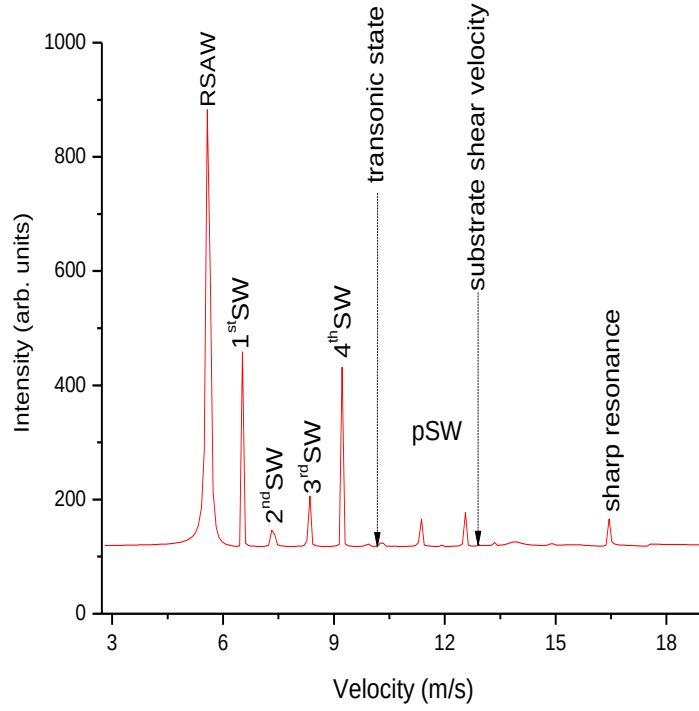


Figure 2.7: Typical SBS spectrum for a thin supported film showing the Rayleigh surface acoustic wave (RSAW), Sezawa waves (SW), pseudo Sezawa waves (pSW) and sharp resonances. These features will be described in detail in Chapter 4.

The solution for the 9 equations for the partial wave amplitudes takes the form

$$A_j^{(n)} = \frac{i}{\omega} (\mathbf{B}^{-1})_j^{(n)}. \quad (2.67)$$

Using (2.67), the displacement Green's function at the surface can be obtained from (2.54) and is given by

$$G_{33}(\mathbf{x}_{\parallel}, x_3 = -d, t) = \int_{-\infty}^{\infty} \frac{d^2 q_{\parallel}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left\{ \frac{i}{\omega} \sum_{n=1}^6 (\mathbf{B}^{-1})_3^{(n)} U_3^{(n)} \exp(-iq_3^{(n)} d) \right\} \exp i(\mathbf{q}_{\parallel} \cdot \mathbf{x}_{\parallel} - \omega t) \quad (2.68)$$

By taking the Fourier transform of Eq. (2.68), we arrive at the normal component of the Fourier domain elastodynamic Green's function that determines the Brillouin spectrum for the free surface of the layer

$$\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega) = \sum_{n=1}^6 \frac{i}{\omega} (B^{-1})_3^{(n)} U_3^{(n)} \exp(-iq_3^{(n)} d). \quad (2.69)$$

$U_3^{(n)}$ and $q_3^{(n)}$ are respectively, the components of the mode polarization and the frequency dependant wave vector perpendicular to the film plane and d is the film thickness. $n = 1, \dots, 6$ refers to partial waves in the layer and $n = 7, 8, 9$ to outgoing partial waves in the substrate. A true surface wave (RSAW) arises when the inverse of the boundary value matrix B^{-1} becomes singular and then a sharp line in the spectrum is visible. The nature and type of the excitations observed in thin supported films depend on the combination of the overlayer and the substrate. For example Sezawa modes are observed for a slow on a fast system. This will be discussed further in Chapter 4.

Figure 2.7 shows a typical SBS spectrum for a thin film. Elastic constants for thin films are extracted by simultaneously fitting the dispersion curves for the observed modes (Rayleigh and Sezawa) as a function of the product of phonon wave vector parallel to the surface and layer thickness (i.e. v vs $q_{\parallel}d$).

Experimental arrangement for surface Brillouin scattering

3.1 Introduction

Surface Brillouin scattering (SBS) exploits the light scattering technique to investigate the properties of near opaque materials; it permits the study of thermally induced surface acoustic waves at the surfaces of either homogenous solids or thin supported films. Light is not the driving force producing these fluctuations, but it is the tool used to detect them. Laser light is suitable for this purpose because it is intense, monochromatic, highly collimated and highly polarised. The underlying principle of a laser, its design and the theory behind the laser action are discussed in Section 3.2. The section follows closely the instruction manual for Spectra-Physics Model 2060/2080 Ion Laser. In Section 3.3, the auxiliary optics necessary for the backscattering geometry used in SBS are presented. A detailed description of the Tandem Fabry-Pérot interferometer (TFPI) used for this work is given in Section 3.4 which follows closely the operator manual for JRS Scientific Instruments Tandem

Fabry-Pérot Interferometer. The SBS experimental configuration in the backscattering geometry is shown in figure 3.1.

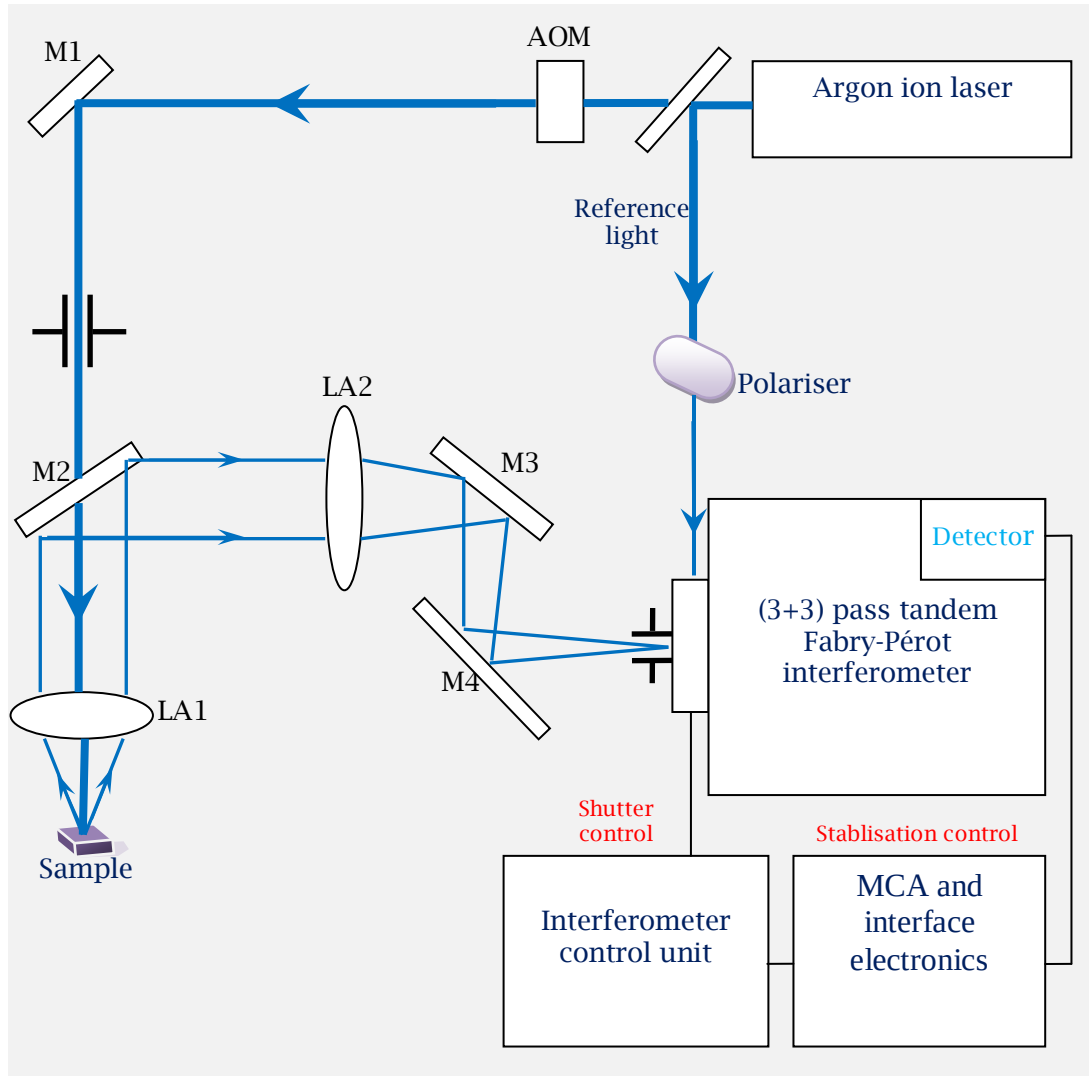


Figure 3.1: Schematic diagram of the experimental arrangement used for surface Brillouin scattering spectroscopy. AOM and MCA stand for acoustic optic modulator and multi-channel analyser, respectively. M and LA represent mirrors and lenses, respectively.

3.2 Laser

The green line of wavelength 514.5 nm, generated by an argon-ion laser operated in a single axial mode was the source of the incident photons for this work and the spectrum of the scattered light from the specimen was examined.

The laser beam is produced through a process called stimulated emission. The name *laser* is an acronym of *light amplification by stimulated emission of radiation*.

3.2.1 Emission and absorption

Emission and absorption of light takes place within the atomic or molecular structure of materials. Figure 3.2 is a schematic energy diagram representing the atomic energy levels requisite for the laser action. The ground state is the level with the lowest possible energy and the other levels are excited states. An atom in the ground state will stay there until it is excited by an external energy source.

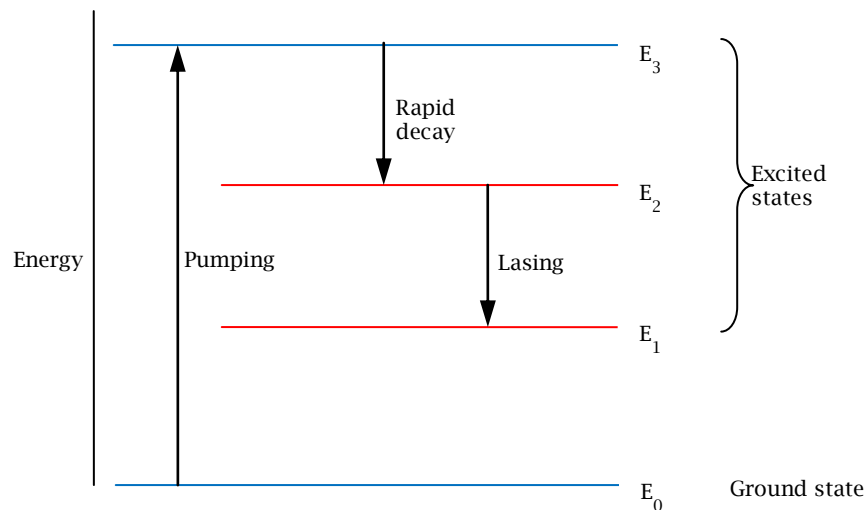


Figure 3.2: Schematic representation of a four-level laser transition scheme

There is however a finite probability per unit time that an atom in excited state 2 will at some later time emit radiation by returning to a lower level 1, radiating a photon of frequency ν

$$\nu = \frac{E_2 - E_1}{h}, \quad (3.01)$$

where h is the Planck's constant. This process is described as spontaneous emission and it occurs even in the absence of an external radiation field. On the other hand, an atom can absorb energy to make a transition from a lower energy state E_1 to a higher level E_2 . This occurs when a photon strikes an atom with exactly the energy to induce an electronic transition between the two energy states. This process is referred to as absorption.

Emission can occur in two ways, it can be spontaneous or stimulated. In spontaneous emission an atom randomly emits radiation in any direction while for stimulated emission, an atom interacts with a photon having energy ($h\nu$) equal to the energy difference ($E_2 - E_1$) between the two levels causing the atom to de-excite to the lower state. This latter process is accompanied by the creation of a second photon, which has identical phase, frequency and direction as the incident one.

3.2.2 Laser design

To produce a laser, one must collimate the stimulated emission. This is done by properly designing a highly reflective cavity. A gain medium, a material with properties that allow amplification of light by stimulated emission, is then introduced

inside the optical cavity. In its simplest form a cavity consists of two mirrors arranged such that light bounces back and forth, each time passing through the gain medium. The gain medium can be a solid, liquid or gas having metastable states in its atoms or molecules. The medium absorbs pump energy, which raises electrons into higher energy quantum states. The energy is typically supplied as an electrical current or as light at different wavelength. If the pump source is intense enough a population inversion may be obtained, i.e., a situation characterised by the presence of more electrons in the metastable state than in the ground state. In this case the rate of stimulated emission is larger than the rate of absorption. Hence, the light is amplified as it passes through the medium.

The frequency spectrum of a free running ion laser consists of a large number of oscillating modes of the optically resonant laser cavity. The resonant laser cavity directs the radiation produced by the gain medium between the cavity mirrors back and forth many times through the medium so that the gain by stimulated emission exceeds the losses. One of the two cavity mirrors (the output coupler) is made slightly transmitting to allow some energy stored within the cavity to be transmitted, and the escaping radiation becomes the output beam.

Gas lasers can be classified into three different types depending on the nature of the energy levels at which the lasing action takes place. In helium-neon and helium-cadmium lasers a transition between unionized atomic states is involved. Carbon dioxide lasers use levels which arise from molecular rotations and vibrations, and the argon and krypton lasers utilize transitions between ionized states.

3.2.3 Argon ion laser

The properties of the argon-ion (Ar^+) laser are probably the most understood of all the ionized gas laser media. In order to singly ionize argon atoms, a considerable amount of energy must be supplied to the argon gas. Figure 3.3 illustrates the energy level diagram of the argon-ion laser. The neutral atom of energy E_0 , is pumped to the 4p energy level by two successive collisions with electrons. The first ionizes the atom and the second subsequently excites the ion from its ground state E_1 either directly to the 4p energy level, E_3 , or to even higher energy states, E_4 , from where it non-radiatively de-excites to the metastable state 4p (E_3).

The 4p state ions eventually decay to the 4s (E_2) level by emitting a photon either spontaneously or by stimulated emission. The 4s level is sufficiently high above the ground state; therefore it will be effectively empty, so a comparatively small population in the 4p state is needed to ensure a population inversion between 4p and 4s. Laser action thus takes place between these levels.

The laser gain is strongly dependent on gas pressure. The cw argon-ion laser operates with a gas pressure of approximately 0.3 torr and 240 V discharge voltage. For SBS experiments discharge currents of up to 30 A which yields laser output power of up to 600 mW are commonly used. Considerable higher output powers maybe achieved with higher discharge currents.

Two argon-ion lasers, a Model 2060 Spectra-Physics and a Coherent Innova 300 were used in the present work, with the former being used for most of the work.

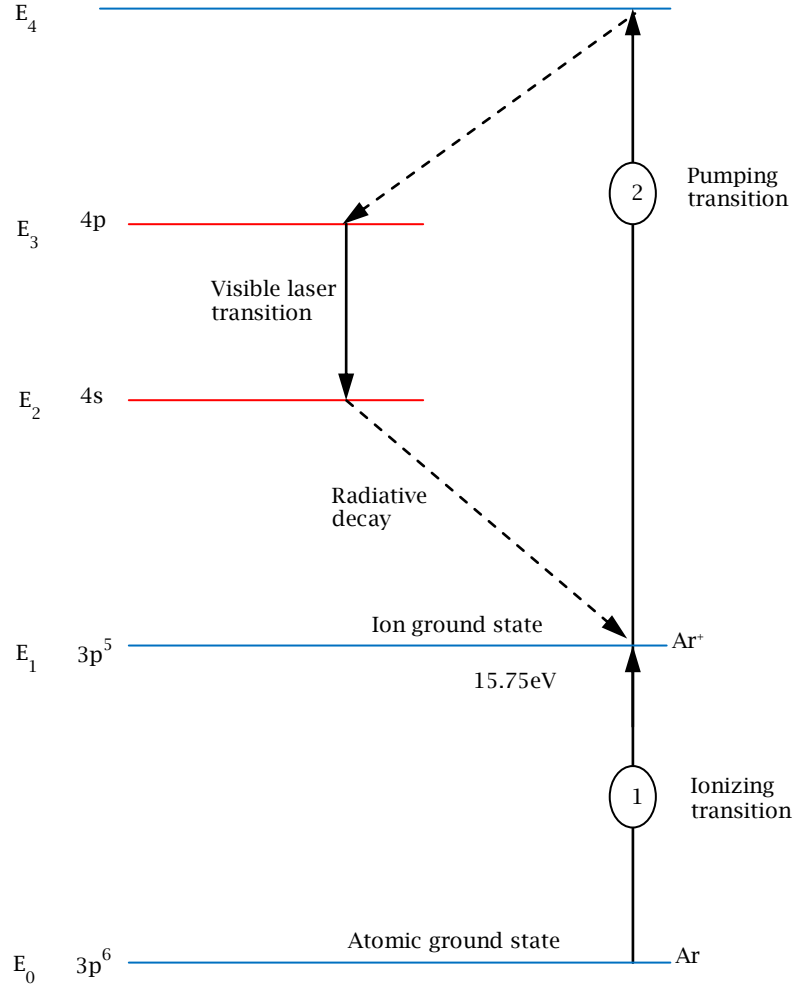


Figure 3.3: Transitions involved in laser action by the Ar^+ ion. (After the instruction manual for the Spectra-Physics Model 2060/2080 Ion Laser).

3.2.4 Intra-cavity etalon

SBS experiments require an extremely narrow laser line width. It is therefore necessary to select a single longitudinal mode whose width is about 3 MHz from the

laser gain profile. To achieve this, a Spectra Physics Model 587 temperature-stabilized intra-cavity etalon is used for the Model 2060 Spectra-Physics argon ion laser and a Coherent Model 300 etalon for the Coherent Innova 300 laser. The etalon serves as a weak loss mechanism in the laser cavity and so inhibits oscillations in all but one frequency.

As discussed in Section 3.2.2, the frequency spectrum of a free running ion laser consists of a large number of oscillating modes of the optically resonant laser cavity. The oscillations in the cavity can be limited to only one single line wavelength by adding a prism to the cavity. The dispersion of the prism allows only one line to be perfectly aligned with the high reflector enabling one to choose a line by simply tilting the prism. For a single line, the laser oscillates around a transition frequency within a narrow range. Thus, the output of a given line is a set of discrete frequencies called longitudinal modes. The frequency distribution of the longitudinal modes is shown in figure 3.4. The distribution depends on the gain medium, the plasma temperature and the magnitude of the population inversion. In order to isolate a single longitudinal mode, a broad-band filter is added to the cavity. Both the Spectra Physics and Coherent lasers utilize an intra-cavity Fabry-Perot etalon, which acts as a broad-band, low-loss, optical filter. The etalon introduces sufficient losses in all frequencies other than the one selected (Fig. 3.5). It is typically made of two parallel reflecting surfaces. The partial reflectors create multiple overlapping beams which are intentionally directed out of the cavity by a small tilt of the etalon with respect to the laser beam and hence are suppressed.

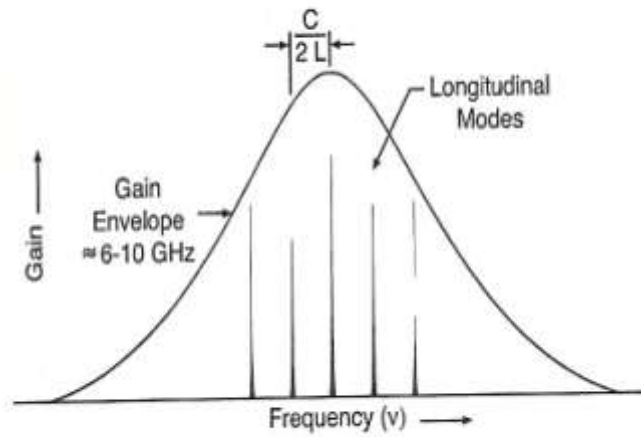


Figure 3.4: The frequency distribution of longitudinal modes for a single laser line
(After the instruction manual for the Spectra-Physics Model 2060/2080 Ion Laser.)

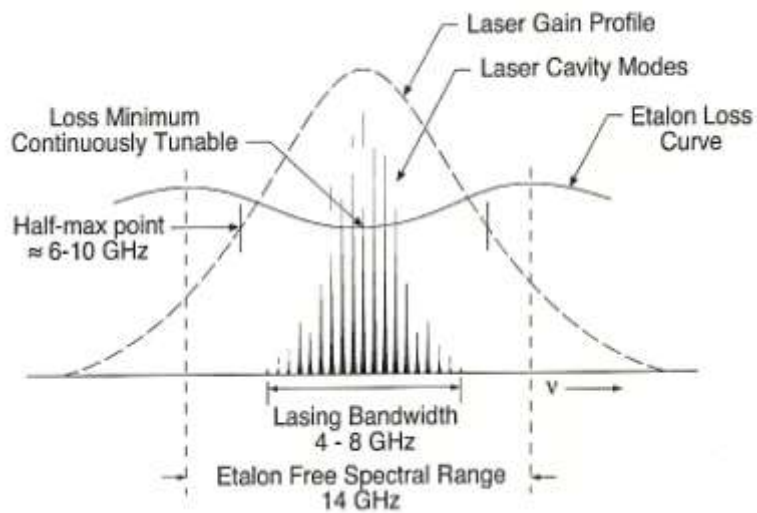


Figure 3.5 Etalon loss minimum tuned to laser gain maximum (After the instruction manual for the Spectra-Physics Model 2060/2080 Ion Laser.)

The losses arise as a result of the fact that the displaced beams do not overlap completely with the fundamental resonator beam. The light that is reflected out of the cavity when the off-peak modes are active is therefore the loss induced by the etalon. To facilitate just one cavity mode into oscillation the frequency difference between the etalon loss minima or maxima should be greater than the width of the laser gain profile. Figure 3.5 shows an etalon loss curve superimposed on a laser gain profile illustrating the etalon loss minimum being tuned to the laser gain maximum.

3.3 Auxiliary optics

The back scattering arrangement shown in figure 3.6 was used for this work. The laser beam is passed through a 2 mm diameter hole, drilled through the centre of an elliptical mirror M2 onto a 120 mm focal length lens LA1 of aperture f/5.5. The doublet achromatic lens LA1 focuses the laser beam onto the sample surface and simultaneously collects and collimates the scattered light from the sample surface. The scattered light in a parallel beam from LA1 is focused onto the entrance pinhole P2 of the interferometer by a second achromatic lens LA2 of focal length 400 mm. The two steering mirrors M3 and M4 provide additional degrees of freedom for alignment purposes. The mirrors are dielectric coated so as to have minimum insertion loss.

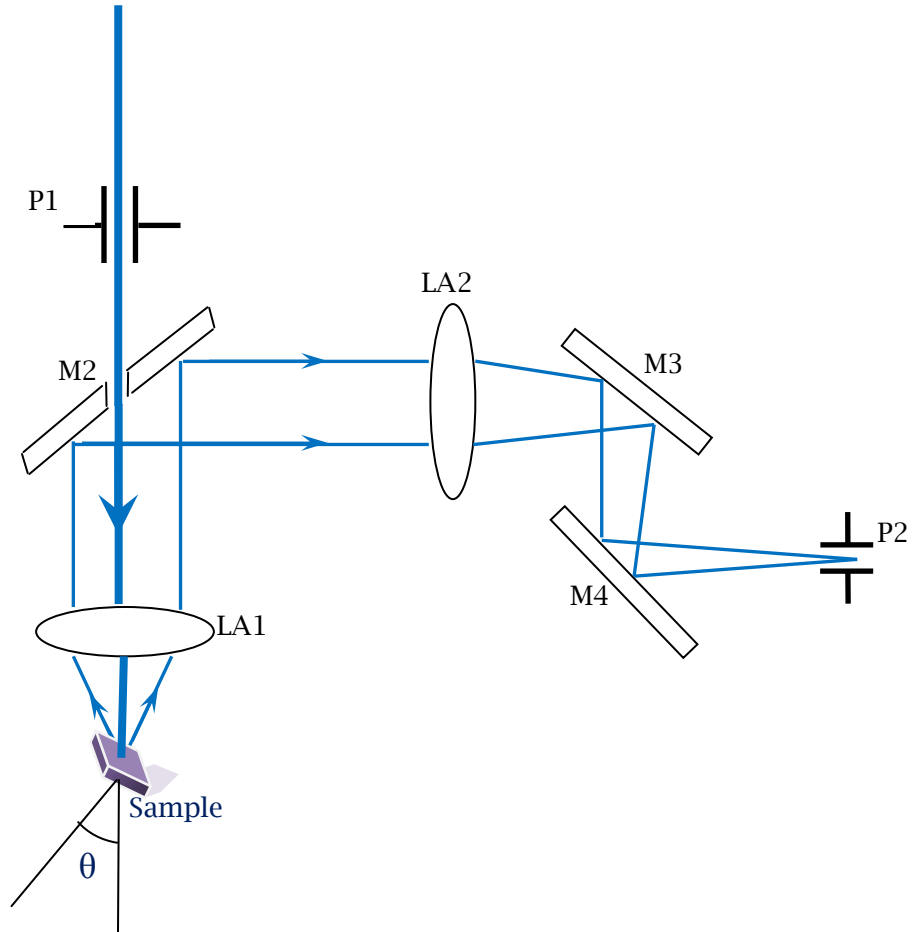


Figure 3.6: Backscattering geometry defined for SRS experiments, where P1 is an aperture, M2 is the elliptical mirror, LA1 and LA2 are lenses, M3 and M4 are steering mirrors and P2 is the entrance pinhole to the interferometer.

The scattering cross section from thermally excited acoustic waves is small. As a result the weak Brillouin signal (from the inelastically scattered light) is simultaneously present with the elastically scattered light that is intense. It is therefore necessary to limit the elastically scattered light so as to prevent destruction of the detector. On the other hand it is necessary to inject a fixed intensity reference signal during the interferometer scan in order to stabilise the instrument. This is achieved by a shutter system, provided by JRS Scientific Instruments, inserted in front of the entrance pinhole. The shutter automatically switches to the reference signal during the region of the interferometer scan corresponding to the transmission of the elastically scattered light. This avoids possible overload by the strong elastically scattered light and damage to the detector. A polarizer (Fig. 3.1) in the path of the reference beam allows its intensity to be optimally adjusted.

3.4 Tandem Fabry-Pérot Interferometer

3.4.1 Introduction to Fabry-Pérot Interferometry

The Fabry-Pérot interferometer (FP) was first introduced in 1897 by the French physicists Charles Fabry and Alfred Pérot. It is an optical instrument which uses multi-beam interference by utilizing the fringes produced in the transmitted light (Born and Wolf, 1975). The light is transmitted after multiple reflections in the air-film interface between two plane mirrors mounted accurately parallel to one another. The two parallel highly reflecting mirrors constitute an assembly referred to as an

etalon. Because of the high reflectivity of the parallel mirrors, the successive multiple reflections of light waves diminish very slowly in intensity and form very narrow sharp fringes which may be used to reveal hyperfine structures in line spectra.

The varying transmission function of an etalon is caused by the interference between the multiple reflections of light between the two reflecting surfaces. Constructive interference occurs if the transmitted beams are in phase and destructive interference when they are out of phase. Constructive interference corresponds to a high-transmission peak of the etalon whilst destructive interference corresponds to a transmission minimum.

The phase difference (δ) between each successive reflection is given by the expression

$$\delta = \left(\frac{2\pi}{\lambda} \right) 2nl_1 \cos \theta, \quad (3.02)$$

where l_1 is the mirror spacing of the etalon and n is the refractive index of the material between the reflecting surfaces (Fig. 3.7), which in this case is air. If both surfaces have reflectance R , the transmitted I_t and reflected I_r intensities are given by the following expressions;

$$\frac{I_t}{I_i} = \frac{1}{1 + Q_R \sin^2 \frac{\delta}{2}}, \quad (3.03)$$

$$\frac{I_r}{I_i} = \frac{Q_R \sin^2 \frac{\delta}{2}}{1 + Q_R \sin^2 \frac{\delta}{2}}, \quad (3.04)$$

where

$$Q_R = \frac{4R}{(1-R)^2}, \quad (3.05)$$

is the quality factor for reflectivity usually known as the finesse coefficient and I_i is the intensity of the incident light. Q_R is related to the finesse F of the etalon by

$$F = \frac{\pi \sqrt{Q_R}}{2}. \quad (3.06)$$

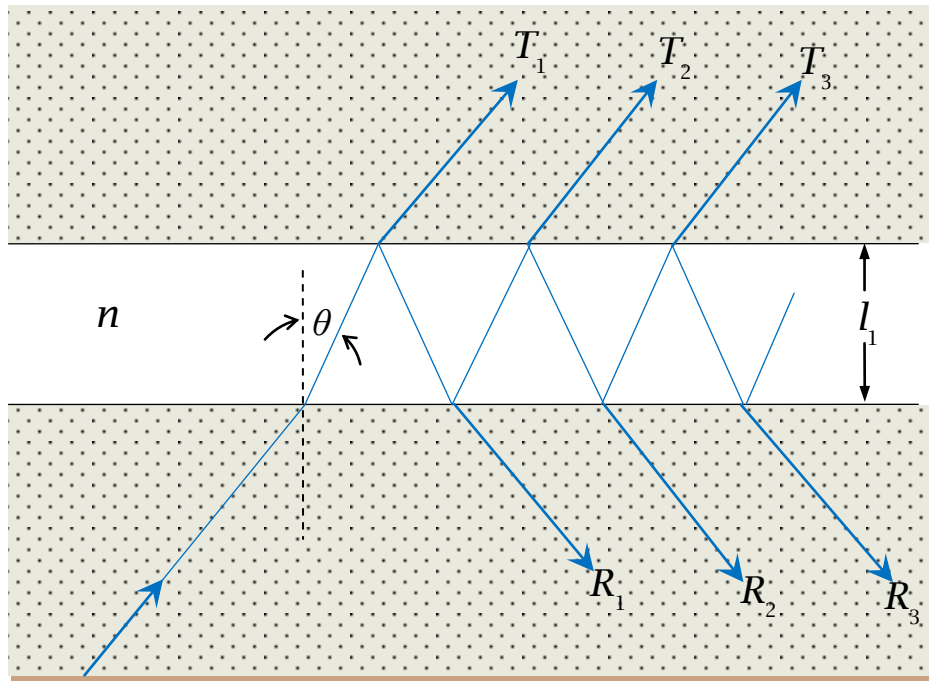


Figure 3.7: The reflection of a plane wave in a plane parallel plate, Fabry-Pérot etalon.

Using equations (3.02), (3.03), (3.05) and (3.06) it can be shown that the interferometer will only transmit certain wavelengths determined by

$$T = \frac{\tau_0}{1 + \left(\frac{4F^2}{\pi^2} \right) \sin^2 \left(\frac{2\pi L_1}{\lambda} \right)}, \quad (3.07)$$

where $\tau_0 (< 1)$ is the maximum possible transmission and $L_1 = nl_1$ is the optical spacing of the mirrors. Equation (3.07) shows that only wavelengths satisfying

$$L_1 = \frac{1}{2} m \lambda \quad \text{where } m = 1, 2, 3, \dots \text{ is an integer,} \quad (3.08)$$

will be transmitted.

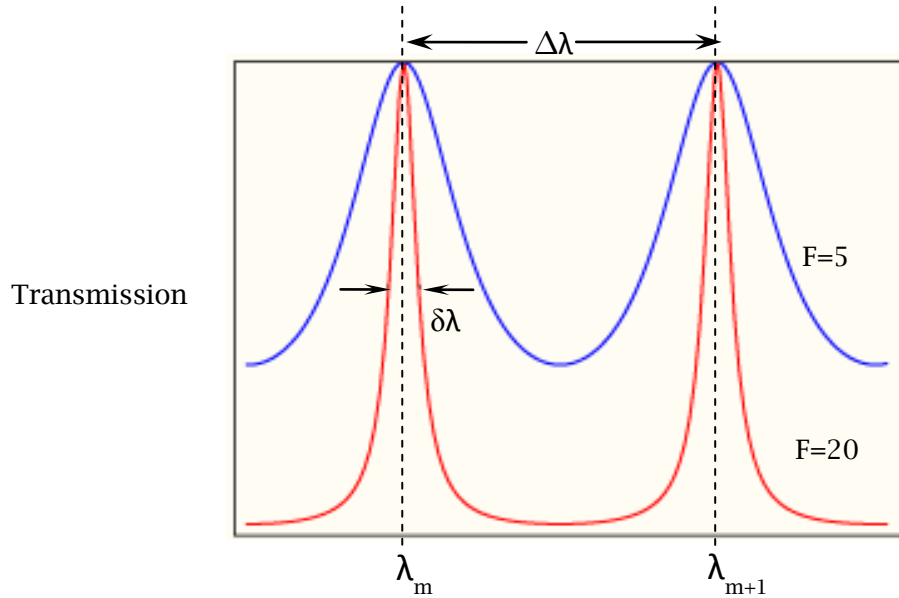


Figure 3.8: Transmission of the interferometer as a function of wavelength

The wavelength separation between adjacent transmission peaks $\Delta\lambda$ (also known as the free spectral range, FSR) is given by the expression:

$$\Delta\lambda = \frac{\lambda^2}{2L_1} , \quad (3.09)$$

and it is related to the full width at half-maximum, $\delta\lambda$, of any one transmission band and the finesse F by

$$F = \frac{\Delta\lambda}{\delta\lambda} . \quad (3.10)$$

A higher finesse etalon ($F=20$ in figure 3.8), shows sharper peaks and lower transmission minima than a lower finesse etalon ($F=5$). Equations (3.09) and (3.10) show that one can make the finesse value large by making $\Delta\lambda$ arbitrarily large by decreasing L_1 . On the other hand $\delta\lambda$ increases proportional to $\Delta\lambda$ and so results in the reduction of resolution. However one can overcome this problem and have a fixed resolution by using a tandem Fabry-Pérot interferometer (Section 3.4.2). In practice the finesse value cannot be made greater than 100 due to limitations on the quality of mirror surfaces and coatings.

High transmission is only possible when certain conditions for the wavelength of light and the plate geometry are fulfilled; otherwise light is more or less blocked. The geometrical conditions are defined by several properties including the mirror spacing, refractive index, and beam direction. To use the Fabry-Pérot interferometer, one of the geometrical properties has to be adjustable and be related in a suitable way to wavelength variations. One can either have an air-spaced interferometer, where spacing or air pressure are used for tuning or alternatively one can use a scanning FP

interferometer in which one of the two reflecting plates is mechanically moved during scanning. In the present SBS experiments scanning FP interferometers are used.

3.4.2 The Tandem Fabry- P rot Interferometer (TFPI)

The problem of FSR, highlighted in Section 3.4.1 can be overcome by using two FP interferometers in series. This ensures an increased FSR at a fixed resolution as shown figure 3.8. The two interferometers have to be synchronised so that the interference maxima for all wavelengths coincide in the spectral region of interest. The optical spacings for FP1 (L_1) and FP2 (L_2) are independently set so as to transmit a given wavelength such that the combined transmission for light passing successively through both FP1 and FP2 is as shown in figure 3.9.

From equation (3.08) the transmission condition for both mirrors is

$$L_1 = \frac{1}{2} m \lambda, \quad L_2 = \frac{1}{2} n \lambda, \quad (3.11)$$

where m and n are integers. However, small intervening transmission peaks normally known as ghosts remain since the transmission of either interferometer never falls to zero as shown in Eq. (3.07). To suppress these neighbouring orders better and to enhance the contrast of the FP interferometer the tandem principle is combined with the multi-pass technique.

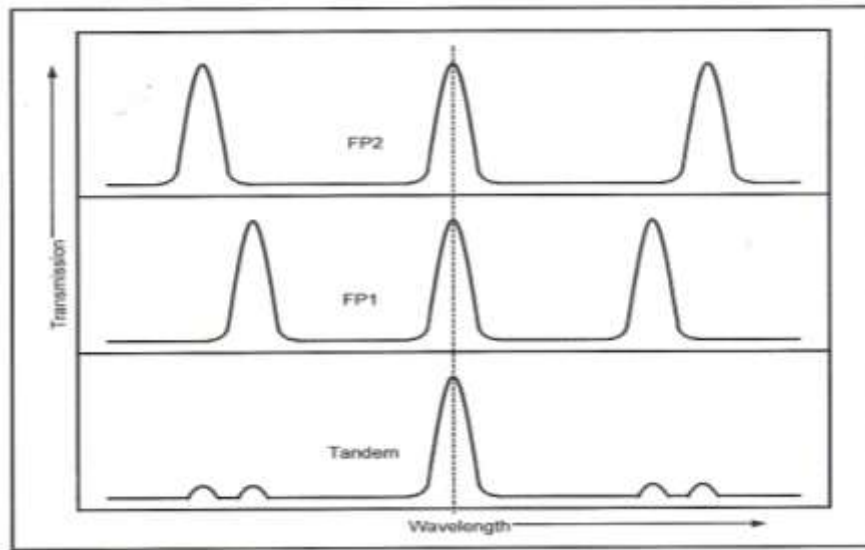


Figure 3.9: Interferogram of a monochromatic spectral line measured by a tandem interferometer (After Mock et. al.,1987).

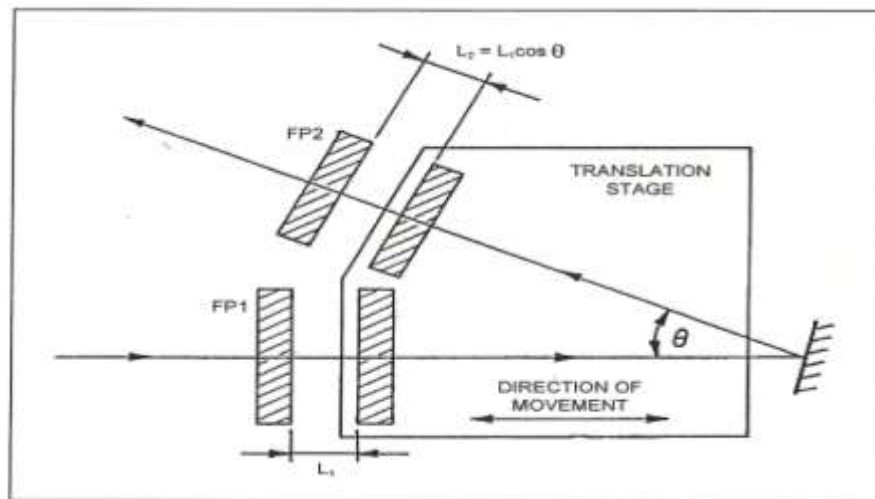


Figure 3.10 The principle of tandem scan (after JRS Scientific Instruments, TFPI operator manual).

There is a danger that a spectral component at $\lambda + d\lambda$ will also be suppressed. Given a small scan in mirror spacings dL_1 and dL_2 , a spectral component $\lambda + d\lambda$ will be transmitted if

$$dL_1 = \frac{1}{2} m d\lambda \quad \text{and} \quad dL_2 = \frac{1}{2} n d\lambda. \quad (3.12)$$

This will only occur if the ratio

$$\frac{dL_1}{dL_2} = \frac{L_1}{L_2}, \quad (3.13)$$

is maintained. It has been demonstrated that by multi-passing, one can achieve a contrast of greater than 10^9 , five or six orders of magnitude greater than that of a single interferometer (Dil *et al.*, 1981; Sandercock, 1982; Mock *et al.*, 1987). In the JRS Instruments tandem interferometer employed for the present SBS measurements, a 3+3 pass arrangement is used in which light passes through each of the two FP's three times before being transmitted to the detector.

3.4.3 Design of the scanning TFPI

The principle of the tandem scan is shown in figure 3.10 above. The two interferometers are mounted on a single scanning stage to obtain both statically and dynamically stable synchronisation. One mirror from each Fabry-Pérot interferometer, FP1 and FP2, are mounted together on the translation stage. Scanning is made possible by the use of piezoelectric actuators which can be driven at moderate voltages (100... 500 V), to obtain a linear scan. It can be seen that, (Fig. 3.10) the axis of FP2 lies at an angle θ to that of FP1 and the two

interferometers will only scan synchronously if the relationship $L_2 = L_1 \cos \theta$ is accurately maintained. In general there will be some error, ε , in the scanning, so that $L_2 = L_1 \cos \theta + \varepsilon$. The spacings of the individual FP mirrors are set such that a movement of the translation stage to reduce the respective mirror spacings would in principle bring both sets of mirrors into simultaneous contact, giving $\varepsilon = 0$. Therefore a small scan dL_1 would then change the spacing of FP1 by dL_1 , and that of FP2 by $dL_1 \cos \theta$. As a result the condition (3.13) is satisfied for the interferometers to scan synchronously.

3.4.4 Vibration isolation and stabilization

A FP arrangement is very sensitive with regard to building vibrations. It requires a quiet, vibration-free environment. Dynamic isolation systems using feedback control are useful for isolating the interferometer from noisy environments. The optical components of multi-passing the interferometer are mounted directly on the optical table, and the tandem interferometer is mounted on two dynamic isolation mounts (JRS Scientific Instruments, Vibration Isolation System MOD-2). These isolation mounts are compact, stiff and have excellent directional and positional stability. The whole set up is then enclosed to protect it from sound waves which can excite high-frequency resonances in the system. The use of a dynamic vibration isolation platform, a light tight box and an electronic scan stabilization system ensures that the alignment is maintained in both the short and long term.

As discussed in Section 3.4.1, there are two types of scanning interferometers in common use which differ in their scanning means, i.e. pressure scanned instruments and piezoelectric scanning interferometers. In piezoelectric scanning, the non-scanning mirror of each FP interferometer is mounted on correction transducers that allow the alignment of the interferometer to be varied around orthogonal axes. The spectrum is continuously monitored and appropriate alignment made as the interferometer is repetitively scanned. These corrections are performed automatically in a feedback loop. The electronic scan stabilization system used in the present work has been described in detail by Sandercock (1976).

To maintain mirror parallelism, a small positive modulation is applied to the alignment transducer on a given axis for a single scan. The polarity is reversed in the subsequent scan. The difference in amplitude of the control peaks arising between the two successive scans is used as a correction voltage applied to the alignment transducer. The following two scans are then used to correct the next axis. This procedure continues as the interferometer is repeatedly scanned. In this way, the instrument will sequentially check and correct the X and Y axes of FP1, followed by the X and Y axes of FP2. The correct mirror spacing is maintained in similar fashion, whereby for absolute mirror spacing, a correction voltage is applied to the Z axis so as to maintain the control peak exactly at the midpoint of the scan. Relative spacing is maintained by applying a correction voltage to all the alignment transducers of FP2.

3.5 Experimental aspects

3.5.1 Daily set up for SBS measurements

For each experiment, the specimen was illuminated with the 514.5 nm line from an argon-ion laser and the spectrum of the scattered light was examined. The incident laser light beam was of power 300 – 400 mW laser and was linearly polarised in the plane of incidence in all cases. In the backscattering arrangement (Fig. 3.6) used, a 120 mm focal length lens of aperture $f/5.5$ is used both for focusing the laser light onto the sample and for collecting the scattered light. The scattered light is analysed by the tandem interferometer and is then detected by a high efficiency silicon avalanche diode detector (EG&G Optoelectronics Canada SPCM-200-PQ) with a dark count of 1 per second.

3.5.2 Data capture and analysis

SBS spectra were acquired for both thin films and bulk samples in a backscattering configuration, as detailed in Section 3.3. The measurements were performed with the sample in air and at room temperature. Each of the samples was mounted onto a goniometer on which both the azimuthal angle (α) and the incident angle (θ) could be varied. For the thin films, SBS measurements were carried out as a function of both θ (from 30° to 80° with the layer thickness constant at 500 nm) and layer thickness d (from 50 nm to 600 nm with the angle of incident constant at 71°), in order to determine the velocity dispersion curves; v vs $q_{||}d$ (Section 2.4). The in-plane

anisotropy of surface modes in bulk samples were determined by varying α whilst θ was kept at 71° . The Fabry-Pérot interferometer was set up with a finesse of about 100 and a free spectral range (FSR) of 40 GHz. The spectral acquisition time for each sample was about 24 hours on average. The acquisition time strongly depends on the optical alignment of the back-scattered light and the sample surface, so patience needed to be exercised with regard to the measurement period.

The spectra were recorded by a Personal Computer-based multichannel analyser (MCA) interfaced with the TFPI and the detector. The MCA was supplied with software, GHOST v. 6.00 supplied by JRS Scientific Instruments. The software provides an easy way to acquire, save and analyse light spectrum data using an RS-232 communication system to pass the data to a common personal computer. The software includes functions for data analysis, spectrum calibration and curve-fitting. The spectrum calibration function was a development from the old MCA as this facilitated the acquiring of an SBS spectrum in terms of frequency shifts as opposed to channel numbers. Acquiring SBS spectrum in terms of channel numbers had some challenges in calibration as a computer program was required to calculate related frequency per channel to enable the plotting of the spectra in terms of frequency shifts (Mathe, 2008). The other functions, data analysis and curve fitting were hardly used as spectra were always stored in ASCII format and later analysed using ORIGIN LAB v. 8 software.

Chapter 4

Surface Brillouin Scattering Theory of a Supported Titanium Carbide Film

4.1 Introduction

This chapter focuses on the different types of waves observed in a supported titanium carbide film based on dispersion curves obtained using elastic stiffnesses calculated from the averaging methods of Voigt, Reuss and Hill. The observed excitations depend mainly on the over-layer and substrate combination. One can either have a fast on slow system or a slow on fast system. A fast on slow system is one in which the shear bulk wave velocity of the layer is greater than that of the substrate. In most cases this corresponds to an elastically hard film on an elastically soft substrate. The converse is true for the shear bulk wave velocities of a slow on fast system. Density plays an equally important role in determining whether a system is a slow on fast or fast on slow. It is known from previous investigations that in a slow on fast system, it is possible to extract the elastic stiffnesses from SBS spectra since the range of

acoustic excitations is much richer (Djemia *et al.*, 2001; Wittkowski, 2004). The Rayleigh and several orders of Sezawa waves usually provide sufficient information to extract a full set of elastic stiffnesses. However in the case of an opaque fast on slow system, the measurable excitations are few, making it much more difficult to extract the elastic stiffnesses.

The excitations observed in Brillouin spectra of thin supported films in general include among others, the Rayleigh surface acoustic wave (RSAW), pseudo-surface acoustic wave (pSAW), Sezawa waves (SWs), pseudo-Sezawa waves (pSWs), the continuum of excitations resulting from bulk wave interactions with the surface resulting in the Lamb shoulder, Love waves and Stoneley waves. RSAWs and pSAWs have been discussed in chapter 2. SWs are surface waves in which the particle displacements are mainly localised in the layer and falling off exponentially in the substrate. These waves are only observed in a slow on fast system. pSWs are Sezawa-like peaks corresponding to attenuated excitations. Love waves are transverse modes in a layered half-space (Bell *et al.*, 1987) and Stoneley waves are waves that are localised at the boundary between film and substrate (Bell *et al.*, 1988). Several parameters must be taken into account in discussing the Brillouin cross-section profile of a thin film: the transparency of the film, its thickness, the elastic moduli of the film and substrate, and the wave dispersion. The parameters are now discussed in turn.

The transparency of the film determines the scattering mechanism dominant in the film, i.e., elasto-optic scattering or surface-ripple scattering (see Section 2.1.1).

The elasto-optic scattering mechanism is considerably more efficient than the surface-ripple scattering mechanism for transparent films whereas the surface-ripple mechanism is dominant for opaque films. In a transparent or semi-transparent film, sufficiently rich spectral information can be provided so that it is possible to determine the full set of elastic stiffnesses for the film (Nizzoli *et al.*, 1989). In this situation it is also common to observe the longitudinal guided mode in addition to surface waves. This exists when the longitudinal velocity in the film, v_L^F , is less than that in the substrate, v_L^S . Its velocity lies between v_L^F and v_L^S and is much larger than the transverse velocity of the film, v_T^F . Hillebrands *et al.*, (1988) first observed this mode in a ZnSe film on a GaAs substrate.

Successful application of the SBS technique to opaque and near opaque supported film systems depends critically on accurate knowledge of the film thickness (Beghi *et al.*, 1997). Film thickness is important because it identifies a specific length scale, since the phonon velocity depends on the ratio of the acoustic length to the layer thickness. In fact, the term film is used to refer to a structure in which the penetration depth of the surface wave is of the order of, or less than, the thickness of the structure.

The elastic moduli of both the film and substrate are important because the acoustic response of a supported film is strongly influenced by the elastic properties of the substrate. In a fast on slow system (substrate stiffening) the relatively high elastic moduli of the film has a stiffening effect on the RSAW velocity and, with increasing layer thickness this velocity merges into the bulk continuum and the

associated mode becomes a pSAW. In the converse situation of a slow on fast (substrate loading), the relatively lower elastic stiffnesses of the film as compared to the substrate leads to a reduction of the RSAW velocity and the formation of the higher order modes known as SWs and pSWs. Further classifications into strongly and weakly stiffened or loaded systems are possible, depending on the relative shear wave velocities of film and substrate as will be discussed in Sections 4.3 and 4.4.

4.2 Calculations of elastic stiffnesses of TiC films using Voigt, Reuss and Hill methods

This section follows closely the treatment of Nye (1969), Pang (1997), Crowhurst (2001) and Auld (1973).

The stiffness and compliance constants for crystalline materials are normally given with respect to high-symmetry crystal axes. However this may not always be the most convenient choice of axes in some cases and it therefore becomes necessary to consider transformation of the stiffness and compliance constants into other coordinate systems. In the case of thin supported polycrystalline films the effective film elastic constants or stiffnesses are calculated using the preferred orientation of the crystallites. The Voigt-Reuss-Hill averaging procedures are used in the calculations. The Voigt procedure in the calculation of the elastic stiffnesses assumes the strains to be uniform and the stresses to be discontinuous across the crystallites whilst the Reuss procedure in calculating the elastic compliances assumes the converse. The Reuss and Voigt models are subject to certain thermodynamic

reservations. However the Hill model, which is not subject to these thermodynamic shortcomings, yields elastic constants which are the averages of the Voigt and Reuss constants (Salas *et al.*, 2011). The average of the Voigt and Reuss parameters provide useful starting values for minimization procedures in fitting velocity dispersion curves (see Section 6.3). The first step in the procedure for calculating the elastic stiffnesses involves transformation of the elastic stiffness matrix $[C]$ to $[C']$ and elastic compliance matrix $[S]$ to $[S']$ through use of the Bond (1943) stress transformation matrix $[M]$. The matrix $[C]$ and compliance $[S]$ are the starting parameters expressed in the rectangular co-ordinate system $X(x, y, z)$ with z axis parallel to some high-symmetry direction while $[C']$ and $[S']$ are for the film and expressed in a rectangular coordinate system $X'_i(x', y', z')$ with the z' axis parallel to the preferred direction. $[C'']$ and $[S'']$ are expressed in cylindrical coordinates (ϕ, z') in order to calculate the average over all in-plane directions.

4.2.1 Transformation of elastic stiffness and compliances

A 6×6 matrix that is used to transform stress or strain by means of a single matrix multiplication is constructed. Transformation can then be carried out directly in the abbreviated subscript notation (Chapter 1) without converting back to full subscript using an efficient method devised by Bond (1943).

If c_{ijkl} and s_{ijkl} are the fourth rank elastic stiffness tensor and compliance tensor respectively with respect to x_i axes, then c'_{mnop} and s'_{mnop} are the corresponding elastic

tensors with respect to a new coordinate system with $X_i (x', y', z')$ axes and are given by Auld (1973) as

$$c'_{mnop} = a_{mi} a_{nj} a_{ok} a_{pl} c_{ijkl}, \quad (4.01)$$

$$s'_{mnop} = a_{mi} a_{nj} a_{ok} a_{pl} s_{ijkl}. \quad (4.02)$$

In full subscript notation, stress and strain transform according to the following equations

$$\sigma'_{mn} = a_{mi} a_{nj} \sigma_{ij}, \quad (4.03)$$

$$\eta'_{op} = a_{ok} a_{pl} \eta_{kl}, \quad (4.04)$$

respectively. To convert to the Voigt abbreviated notation, each component of either stress or strain must be examined individually. For example, the component of stress σ'_{11} is given by

$$\sigma'_{11} = a_{11}^2 \sigma_{11} + a_{12}^2 \sigma_{22} + a_{13}^2 \sigma_{33} + 2a_{12} a_{13} \sigma_{23} + 2a_{11} a_{13} \sigma_{13} + 2a_{11} a_{12} \sigma_{12}.$$

In abbreviated notation

$$\sigma'_1 = a_{11}^2 \sigma_1 + a_{12}^2 \sigma_2 + a_{13}^2 \sigma_3 + 2a_{12} a_{13} \sigma_4 + 2a_{11} a_{13} \sigma_5 + 2a_{11} a_{12} \sigma_6.$$

The resulting stress transformation equation when this procedure is repeated for each component is

$$\sigma'_I = M_{IJ} \sigma_J, \quad I, J = 1, 2, 3 \dots 6 \quad (4.05)$$

where M_{IJ} are the components of the transformation matrix $[M]$

$$[M] = \begin{bmatrix} a_{11}^2 & a_{12}^2 & a_{13}^2 & 2a_{12}a_{13} & 2a_{13}a_{11} & 2a_{11}a_{12} \\ a_{21}^2 & a_{22}^2 & a_{23}^2 & 2a_{22}a_{23} & 2a_{23}a_{21} & 2a_{21}a_{22} \\ a_{31}^2 & a_{32}^2 & a_{33}^2 & 2a_{32}a_{33} & 2a_{33}a_{31} & 2a_{31}a_{32} \\ a_{21}a_{31} & a_{22}a_{31} & a_{23}a_{33} & a_{22}a_{33} + a_{23}a_{32} & a_{12}a_{33} + a_{23}a_{31} & a_{22}a_{31} + a_{21}a_{32} \\ a_{31}a_{11} & a_{32}a_{21} & a_{33}a_{13} & a_{12}a_{33} + a_{13}a_{32} & a_{13}a_{31} + a_{11}a_{33} & a_{11}a_{32} + a_{12}a_{31} \\ a_{11}a_{21} & a_{12}a_{22} & a_{13}a_{23} & a_{12}a_{23} + a_{13}a_{22} & a_{13}a_{21} + a_{11}a_{23} & a_{11}a_{22} + a_{12}a_{21} \end{bmatrix} \quad (4.06)$$

Similarly the strain transformation equation is given by

$$\eta'_I = N_{IJ} \eta_J, \quad (4.07)$$

where N_{IJ} are the components of the 6×6 matrix $[N]$

$$[N] = \begin{bmatrix} a_{11}^2 & a_{12}^2 & a_{13}^2 & a_{12}a_{13} & a_{13}a_{11} & a_{11}a_{12} \\ a_{21}^2 & a_{22}^2 & a_{23}^2 & a_{22}a_{23} & a_{23}a_{21} & a_{21}a_{22} \\ a_{31}^2 & a_{32}^2 & a_{33}^2 & a_{32}a_{33} & a_{33}a_{31} & a_{31}a_{32} \\ 2a_{21}a_{31} & 2a_{22}a_{31} & 2a_{23}a_{33} & a_{22}a_{33} + a_{23}a_{32} & a_{12}a_{33} + a_{23}a_{31} & a_{22}a_{31} + a_{21}a_{32} \\ 2a_{31}a_{11} & 2a_{32}a_{21} & 2a_{33}a_{13} & a_{12}a_{33} + a_{13}a_{32} & a_{13}a_{31} + a_{11}a_{33} & a_{11}a_{32} + a_{12}a_{31} \\ 2a_{11}a_{21} & 2a_{12}a_{22} & 2a_{13}a_{23} & a_{12}a_{23} + a_{13}a_{22} & a_{13}a_{21} + a_{11}a_{23} & a_{11}a_{22} + a_{12}a_{21} \end{bmatrix} \quad (4.08)$$

If the stress transformation matrix is applied to Eq. (1.08) and using Eq. (4.05) we obtain

$$[\sigma'] = [M] [C] [\eta], \quad (4.09)$$

and from Eq. (4.07) the untransformed strain matrix $[\eta]$, is given by

$$[\eta] = [\eta'] [N]^{-1}. \quad (4.10)$$

Substituting (4.10) into (4.09) yields

$$[\sigma'] = [C'] [\eta'], \quad (4.11)$$

where

$$[C'] = [M] [C] [N]^{-1}, \quad (4.12)$$

is the transformed stiffness matrix. Similarly, the transformed compliance matrix $[S']$ is given by

$$[S'] = [N] [S] [M]^{-1}. \quad (4.13)$$

It can be shown (Crowhurst, 2001) that the inverse of $[N]$ is the transpose of $[M]$, i.e., $[N]^{-1} = [M]^\dagger$ and similarly $[M]^{-1} = [N]^\dagger$. Therefore the transformed stiffness and compliance matrices reduces to

$$[C'] = [M] [C] [M]^\dagger, \quad (4.14)$$

$$[S'] = [N] [S] [N]^\dagger. \quad (4.15)$$

Using the same procedure, we can transform $[C']$ and $[S']$ from x', y', z' axes to cylindrical coordinates (ϕ, z') using the coordinate transformation matrix

$$[a_c] = \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (4.16)$$

The corresponding transformation matrices are

$$[M_c] = \begin{bmatrix} \cos^2 \phi & \sin^2 \phi & 0 & 0 & 0 & \sin 2\phi \\ \sin^2 \phi & \cos^2 \phi & 0 & 0 & 0 & -\sin 2\phi \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \cos \phi & -\sin \phi & 0 \\ 0 & 0 & 0 & \sin \phi & \cos \phi & 0 \\ \cos^2 \phi \sin^2 \phi & \cos^2 \phi \sin^2 \phi & 0 & 0 & 0 & \cos^2 \phi - \sin^2 \phi \end{bmatrix} \quad (4.17)$$

$$[N_c] = \begin{bmatrix} \cos^2 \phi & \sin^2 \phi & 0 & 0 & 0 & 0 \\ \sin^2 \phi & \cos^2 \phi & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & \cos^2 \phi \sin^2 \phi & \cos^2 \phi \sin^2 \phi & 0 \\ 0 & 0 & \sin 2\phi & \cos \phi & -\sin \phi & 0 \\ 0 & 0 & -\sin 2\phi & \sin \phi & \cos \phi & 0 \\ 0 & 0 & 0 & 0 & 0 & \cos^2 \phi - \sin^2 \phi \end{bmatrix} \quad (4.18)$$

The transformed stiffness $[C'']$ and compliance $[S'']$, matrices with respect to cylindrical axes are

$$[C''] = [M_c] [C'] [M_c]^\dagger, \quad (4.19)$$

$$[S''] = [N_c] [S'] [N_c]^\dagger. \quad (4.20)$$

The average stiffnesses and compliances are therefore given as

$$\bar{C}_{\alpha\beta} = \frac{\int_0^{2\pi} C''_{\alpha\beta} d\phi}{2\pi}, \quad (4.21)$$

$$\bar{S}_{\alpha\beta} = \frac{\int_0^{2\pi} S''_{\alpha\beta} d\phi}{2\pi}, \quad (4.22)$$

where $C''_{\alpha\beta}$ and $S''_{\alpha\beta}$ are the relevant elements of matrices $[C'']$ and $[S'']$, respectively.

These averages yield five distinct non-zero constants each, for polycrystalline aggregates with preferred orientation. For stiffnesses, the five distinct average constants are C_{11} , C_{12} , C_{13} , C_{33} and C_{44} . However the general elastic properties of polycrystalline aggregates with a random distribution of anisotropic crystallites of any symmetry classes are the same as those of the isotropic material (Pang, 1997). The TiC films prepared in this work have a random distribution of crystallites with no preferred orientation, as determined from glancing incidence X-ray diffraction

(GIXRD) (Section 5.4.3) results. As a result, only two non-independent elastic stiffnesses (isotropic case, refer to Chapter 1) will be determined for the TiC films instead of five effective elastic stiffnesses (polycrystalline aggregates with preferred orientation).

The single crystal TiC elastic stiffnesses used for calculations are $C_{11} = 513$ GPa, $C_{12} = 106$ GPa and $C_{44} = 178$ GPa (Pang, 1997). The resulting averaged stiffnesses for a TiC film with no preferred orientation as calculated by the Voigt-Reuss-Hill methods are $C_{11} = 492$ GPa, $C_{12} = 116$ GPa and $C_{44} = 188$ GPa. These elastic stiffnesses were used in all the calculations below whose objective was to illustrate the effects of using different substrates in producing a variety of modes.

In the calculations, the acoustic wave vector direction was assumed to be [100] with respect to the (001) plane for all substrates.

4.3 Fast on slow system

The theory of fast on slow or stiffening systems has been developed by a number of workers (Tiersten, 1969; Farnell and Adler, 1972; Alesksandrov *et al.*, 1994; Lefevre *et al.*, 1998; Pang *et al.*, 1999; Zinin *et al.*, 1999.). TiC thin films are elastically hard materials and for many substrates such a supported film constitutes a fast on slow system. TiC has a stiffening effect on the surface-wave velocity because of its relatively high elastic moduli. As the layer thickness is increased the RSAW velocity merges into the bulk continuum and the associated mode becomes a pSAW. A strong stiffening system usually refers to the case where the shear wave velocity of

the film is much higher than that of the substrate, for example a TiC film on Ge substrate. On the other hand a weakly stiffened system refers to a situation where the shear wave velocities of the film and substrate are close to each other with that of the film higher than that of the substrate for example a TiC film on silicon substrate. Simulations of SBS spectra and the velocity dispersion curves of the modes (v vs. $q_{\parallel}d$) for TiC on both germanium and silicon substrates are carried out to illustrate the differences in the spectra.

4.3.1 Acoustic behaviour for a strongly stiffened situation (TiC/Ge)

The elastic stiffnesses used for germanium are: $C_{11} = 129$ GPa, $C_{12} = 48$ GPa, and $C_{44} = 67$ GPa (Bond *et al.*, 1950). Densities used in the calculations are 4.9 g/cm³ and 5.35 g/cm³ for TiC and Ge, respectively. In the case of the TiC film the single crystal density was employed in the illustrative calculations in the absence of available experimental data. Although the experimental studies presented in Chapter 6 demonstrate a lower density in practice, the calculations provide a useful guide to illustrate the various combinations of fast on slow and slow on fast systems. The calculated dispersion relation for wave velocity v vs. $q_{\parallel}d$ and the calculated Brillouin intensities for the TiC/Ge (strong stiffening system) are shown in figure 4.1. This figure depicts $\text{Im}\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega)/\omega$ in a greyscale as a function of $v = \omega/q_{\parallel}$ and $q_{\parallel}d$. In the region $0 < q_{\parallel}d < 2$, the observed mode is the RSAW of the substrate, Ge, which levels off to the shear velocity of Ge at $q_{\parallel}d = 2$. Around, $q_{\parallel}d = 2$, the surface wave

merges into the Lamb shoulder and a highly damped pSAW is evident in the region $2 < q_{||}d < 5$. This is followed by the RSAW of TiC for $q_{||}d$ greater than about 6. In this strong stiffening system, a pre-Rayleigh emerges at the discontinuity around $q_{||}d = 5.2$. This discontinuity is only observed for strong stiffening systems.

Due to the opacity of TiC, the Brillouin intensities (Fig. 4.1) are dominated by the surface ripple mechanism which is proportional to the power spectrum of the vertical displacement component at the free surface. The most intense mode is the RSAW velocity of Ge which merges into the bulk continuum as $q_{||}d$ is increased, to become a pSAW. The mode levels off at the RSAW velocity of TiC, ≈ 5600 m/s. The discontinuity region is clearly visible.

Sharp resonances (higher mode pSAW) and broad resonances may also be observed as the layer thickness is increased (increasing $q_{||}d$) in a stiffening system. For *TiC/Ge* only broad resonances are observed as shown in figures 4.1 and 4.2. The presence of damped resonances above 6500 m/s in the continuum of excitations is observable due to the high stiffening effect of TiC. These are observed as broad peaks in SBS spectra as shown in figure 4.2.

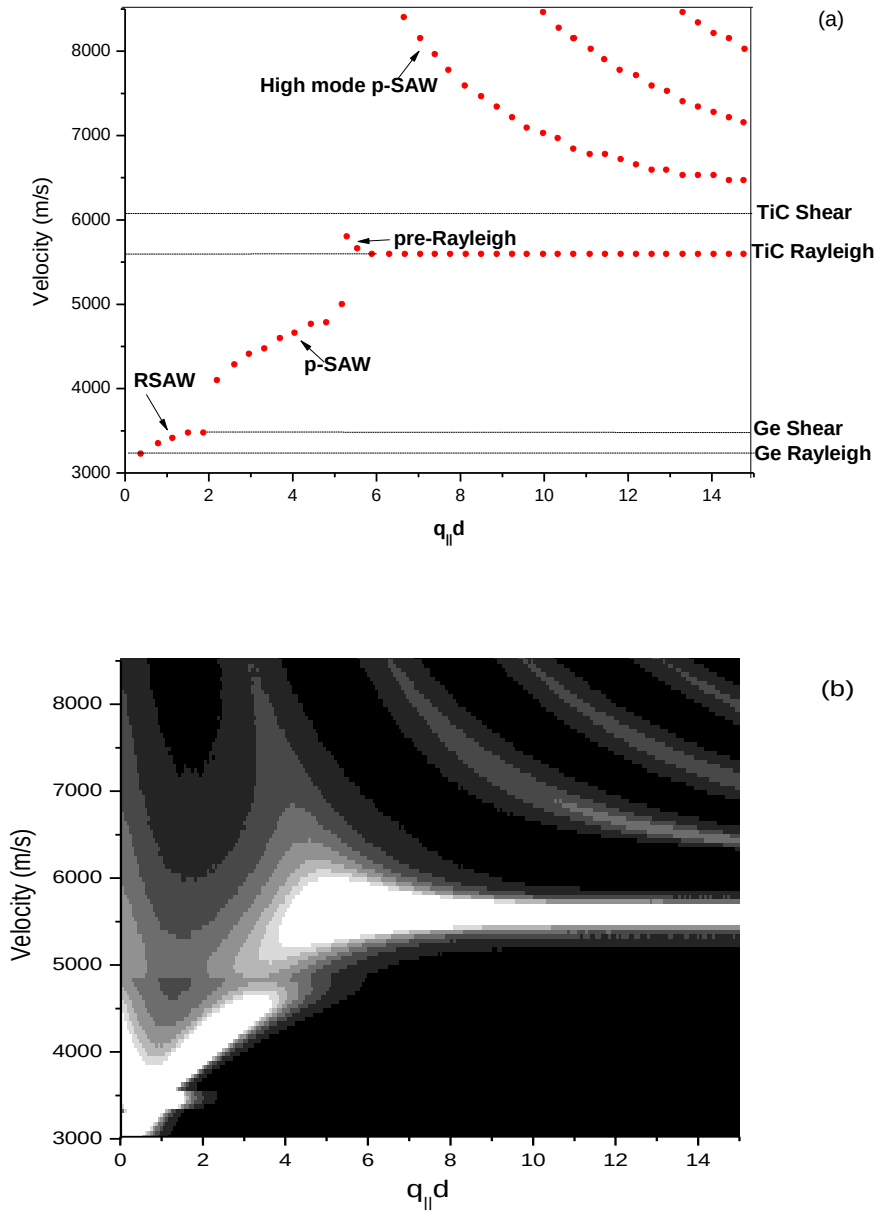


Figure 4.1: (a) Velocity dispersion of the modes vs. $q_{||}d$ for TiC/Ge system. The Brillouin intensities for the same system, calculated by the elastodynamic Green's function using the G_{33} component are shown in (b). This system represents a strong stiffening situation because the shear wave velocity of TiC is about 1.9 times that of Ge. In this situation the Rayleigh mode is the most intense and the discontinuity is clear between the pSAW and pre-Rayleigh.

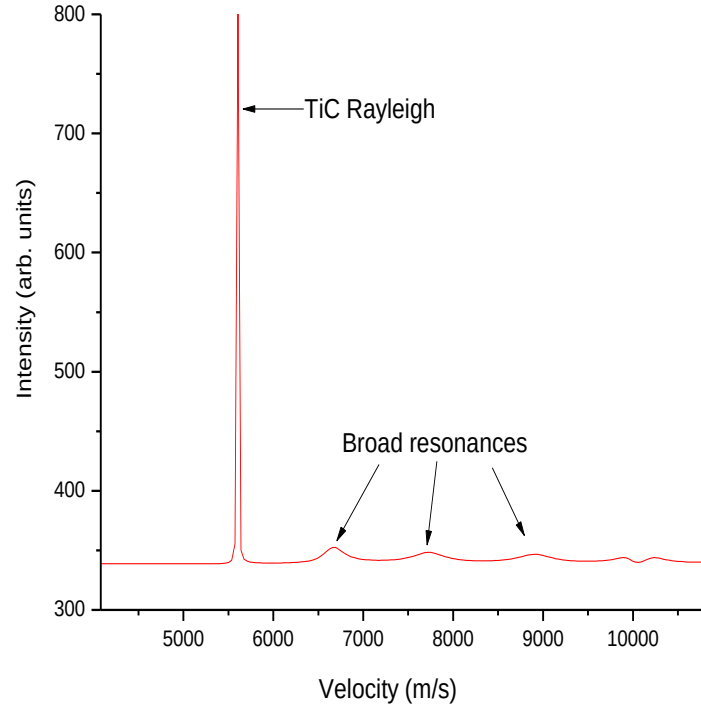


Figure 4.2: Calculated surface-ripple Brillouin spectrum for a 500 nm ($q_{\parallel}d = 11.5$) TiC layer on germanium. An intense RSAW is visible together with broad resonances. Since the signal to noise ratio is very low for broad resonances, it is difficult to observe them experimentally.

4.3.2 Acoustic behaviour for a weakly stiffened situation

(TiC/Si)

The bulk shear wave velocity of materials depends on both the elastic stiffnesses and mass density. Variation in either has an effect on the dispersion relation of a supported film. Because of its low density, silicon has a relatively high shear wave velocity, ≈ 5800 m/s. This is very close to the shear wave velocity of TiC, ≈ 6100 m/s. Hence, a TiC film on a silicon substrate is a perfect example of a weakly

stiffened system. The elastic stiffnesses used for Si are literature values (Zhang *et al.*, 1998) in GPa: $C_{11} = 166$, $C_{12} = 64$, $C_{44} = 80$ and a mass density of 2.2 g/cm^3 .

Figures 4.3 shows the phase velocity dispersion curves v vs. $q_{||}d$ and the calculated Brillouin intensities for the *TiC/Si* system. Comparison of figure 4.1 and figure 4.3 shows that there is no pre-Rayleigh mode appearing in the *TiC/Si* system. In the region $2 < q_{||}d < 8$, the pSAW velocity increases as $q_{||}d$ increases until it levels off at the Rayleigh bulk wave velocity of TiC. No discontinuity of pSAW is identified in this system.

There is a specific low-frequency dispersion observed experimentally in the region $q_{||}d < 2$. The RSAW velocity decreases initially and starts to increase at $q_{||}d = 1$ (Fig 4.3). This was explained by Shuvalov and Every (2002) who studied the properties of SAW in anisotropic-coated solids using the impedance method. In their work, it was reported that for a dense fast on slow system i.e., $\rho^{(l)}/\rho^{(s)} \gg 1$ (where $\rho^{(l)}$ is the density of the layer and $\rho^{(s)}$ is the substrate density), a specific low-frequency dispersion is observed. This is due to the fact that the order of magnitude of the layer impedance $\mathbf{z}$ at $q_{||}d \ll 1$ is proportional to $q_{||}d$. As a result the parameters, $\rho^{(l)}/\rho^{(s)} \gg 1$ and $q_{||}d \ll 1$ become competitive factors at low frequencies.

The densities used in the calculations are; $\rho^{(l)} = 4.9 \text{ g/cm}^3$ and $\rho^{(s)} = 2.2 \text{ g/cm}^3$. Since $4.9 / 2.2 > 1$, the system represents a dense fast on slow system and it is therefore expected for the RSAW velocity to decrease initially before increasing at very low $q_{||}d$ values.

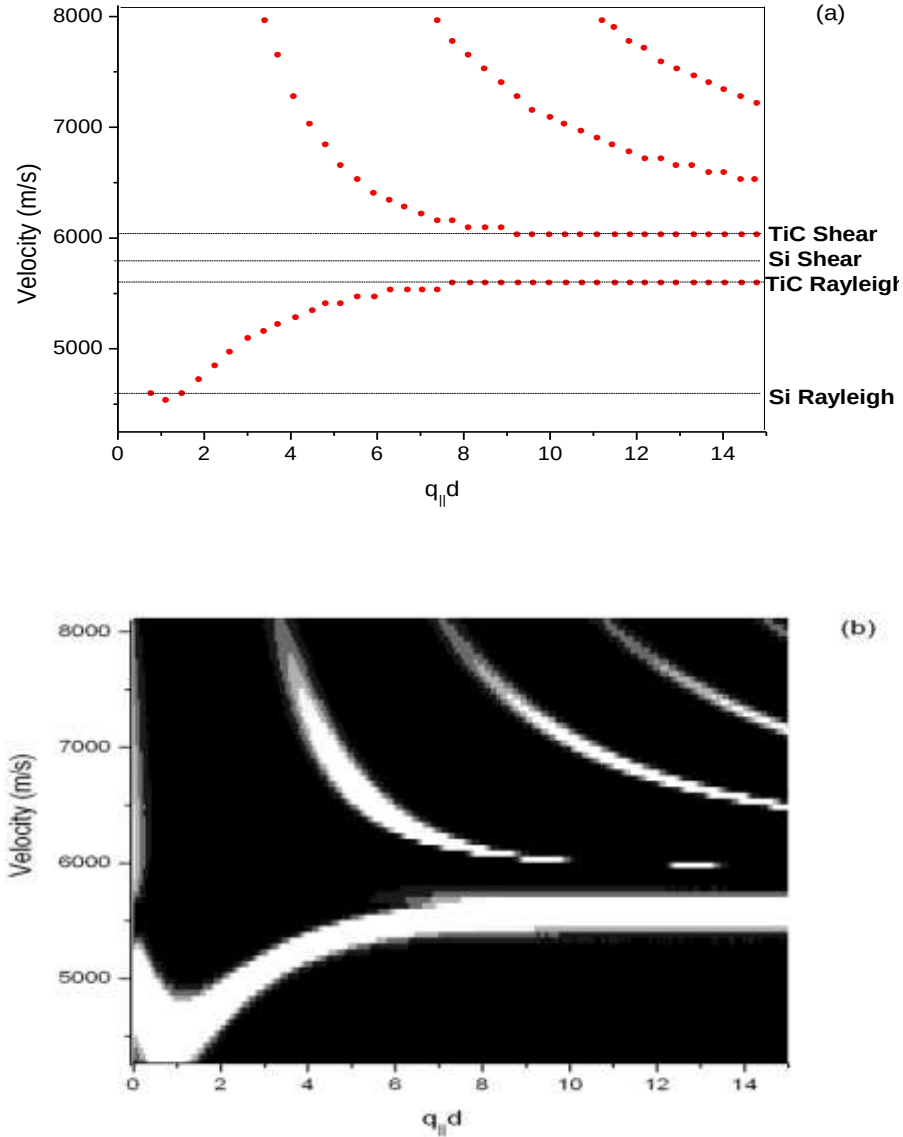


Figure 4.3: (a) Velocity dispersion of the modes vs. $q_{||}d$ for *TiC/Si* system. The Brillouin intensities for the same system, calculated by the elastodynamic Green's function using the G_{33} component are shown in (b). This system represents a weak stiffening situation because the shear wave velocity of TiC is about 1.05 times that of Si. The discontinuity in the pSAW is not observed.

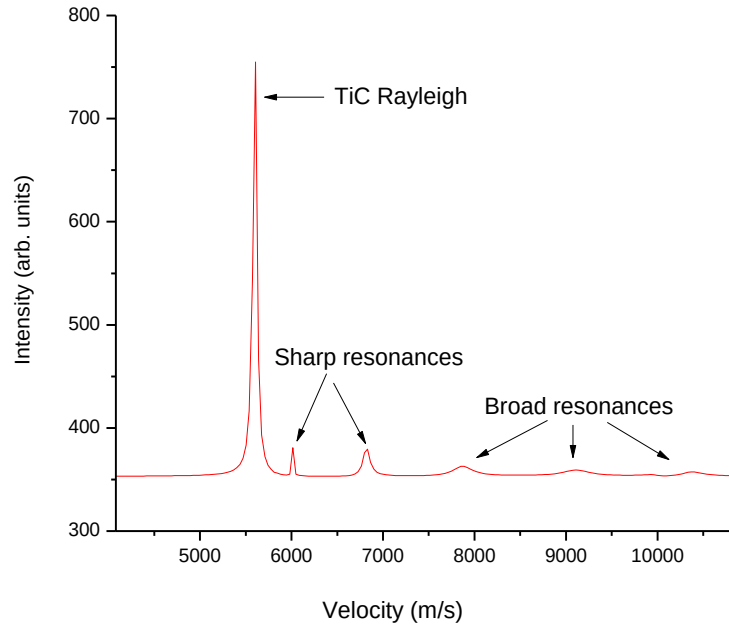


Figure 4.4: Calculated surface-ripple Brillouin spectrum for a 500 nm ($q_{||}d = 12$) TiC layer on silicon. An intense RSAW is visible together with sharp and broad resonances. This is a characteristic of a weakly stiffened system.

Both sharp and broad resonances may be observed as the layer thickness is increased in this weakened stiffening system. Figure 4.4 shows a calculated SBS spectrum for a 500 nm TiC layer on silicon. The sharp resonances are clearly visible together with broad resonances. The sharp resonances can be observed experimentally and can be used in the determination of elastic stiffnesses, especially in cases where the true surface wave data is not adequate to determine the full set of elastic stiffnesses.

4.4 Slow on fast system

The presence of an elastically soft film on an elastically hard substrate leads to a reduction of the RSAW velocity and formation of higher-order modes known as Sezawa and pseudo-Sezawa, as $q_{||}d$ increases. These waves only exist if the shear bulk-wave velocity of the layer is less than that of the substrate. We shall refer to the case where the shear wave velocity of the film is much lower than that of the substrate as a strong loading system. A weak loading system will refer to the case where the shear wave velocity of the layer is approximately equal to that of the substrate, but still less than that of the substrate. Simulations of SBS spectra and the velocity dispersion curves of the modes v vs. $q_{||}d$ for TiC on both diamond (strong loading system) and silicon carbide (weak loading system) substrates are carried out to illustrate the differences in the spectra.

4.4.1 Acoustic behaviour for a strong loading system

(TiC/diamond)

The elastic stiffnesses used for diamond are literature values (Grimsditch and Ramdas, 1975) in GPa: $C_{11} = 1076$, $C_{12} = 125$, $C_{44} = 577$ and a mass density of 3.5 g/cm^3 . As a result of its relatively low elastic moduli as compared to diamond, TiC has a loading effect on the RSAW velocity; with increasing $q_{||}d$ this velocity reduces and levels off at the RSAW velocity of TiC. This situation also leads to the formation of SW and pSW. The calculated dispersion relation for wave velocity v

vs. $q_{\parallel}d$ for the *TiC/diamond* system is shown in figure 4.5. The figure shows $\text{Im}\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega)/\omega$ in a greyscale as a function of $v = \omega/q_{\parallel}$ and $q_{\parallel}d$. The RSAW of TiC is much more intense than the SW curves mainly because the RSAW is concentrated near the film surface to which $\tilde{G}_{33}(\mathbf{q}_{\parallel}, \omega)/\omega$ pertains (Every, 2002).

We have seen, from the discussion on Green's functions in Chapter 2, that the solutions $n = 7, 8, 9$ in the region before the transverse bulk wave (TW) threshold, $\omega_T = q_{\parallel}v_T$, have complex $q_3^{(n)}$ and all waves are true surface waves. In anisotropic cases, these waves are observed before a threshold known as a transonic state. In isotropic cases, this threshold generally coincides with the bulk wave transverse velocity of the substrate, v_T^S . In figure 4.5, six true surface waves (SWs) are observed in the region $2 < q_{\parallel}d < 15$ and are all lying before the transonic state. The region before the transonic state in which true surface wave lies is known as the subsonic region, and the region beyond the transonic state is known as the supersonic region. Pseudo-surface acoustic waves lie in the supersonic region. The pSW behaves like the SW but its bulk-wave component carries energy away from the surface into the interior of the substrate and causes the wave to decay with distance. These waves are more pronounced in the velocity region from the transonic state to v_T^S . In this strong loading system, broad resonances are not observed. Sharp resonances are observed even in the velocity region way above the v_T^S . A typical SBS spectrum (Fig. 4.6) shows all the modes discussed above.

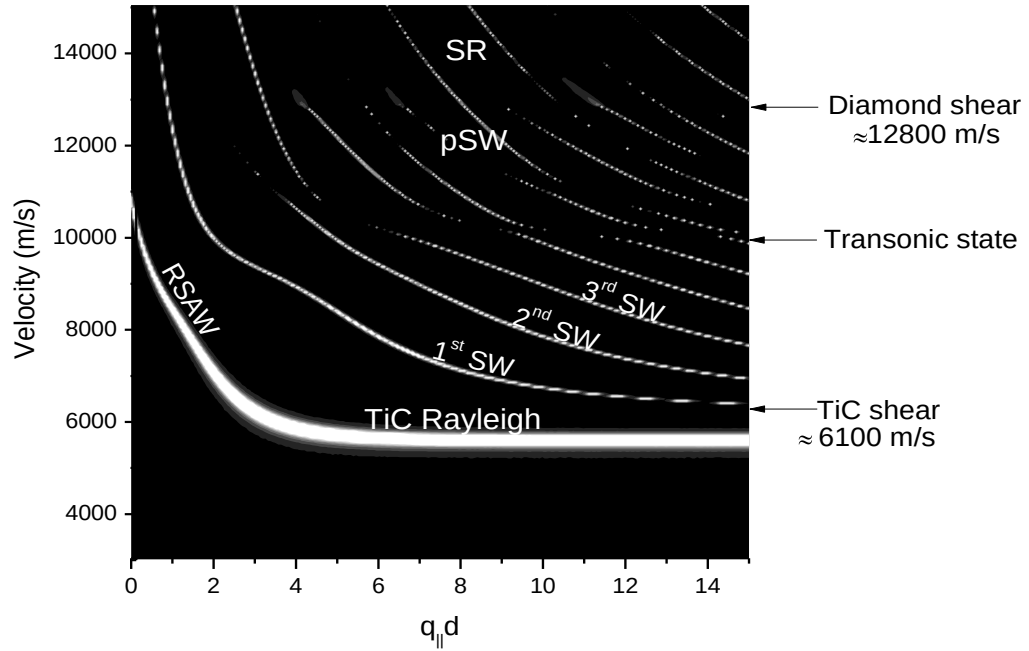


Figure 4.5: Brillouin intensities calculated by the elastodynamic Green's function using the G_{33} component for the *TiC/diamond* system. It shows the dispersion of the RSAW, SW and pSW. 1st SW – first Sezawa wave, 2nd SW– second Sezawa wave, 3rd SW– third Sezawa wave. pSW identifies the pseudo-Sezawa waves region which falls between the transonic state and the shear bulk wave velocity of the substrate. SR identifies sharp resonances observed in the region beyond the shear bulk wave velocity of the substrate.

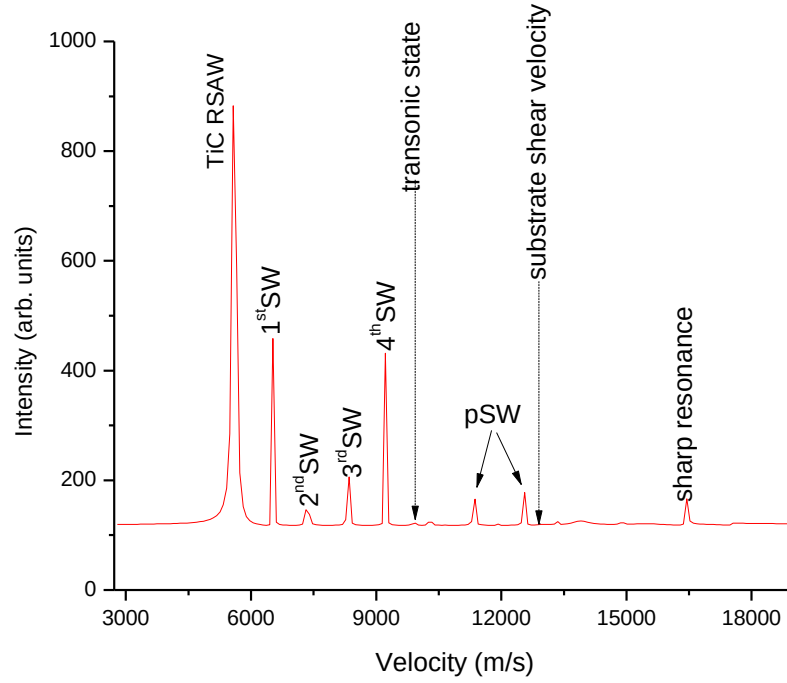


Figure 4.6: Calculated surface-ripple Brillouin spectrum for a 500nm ($q_{||}d = 11.5$) TiC layer on diamond. SW are visible in the velocity region between the RSAW and the transonic state. pSWs are visible in the region between the transonic state and the substrate bulk wave transverse velocity. A sharp resonance is also visible in the supersonic region.

4.4.2 Acoustic behaviour for a weak loading system (TiC/SiC)

The system *TiC/SiC* represents a weak loading situation because the shear wave velocity of TiC is about 0.9 times that of SiC. Thus, the shear wave velocity of the film, TiC, is almost close to and less than that of the substrate, SiC. The elastic stiffnesses used for silicon carbide (SiC) are literature values (Kamitani et al., 1997)

in GPa: $C_{11}=501$, $C_{33}=553$, $C_{44}=163$, $C_{12}=111$, and $C_{13}=52$ and a mass density of 3.2 g/cm^3 .

Figure 4.7 shows velocity dispersion curves of the modes v vs. $q_{\parallel}d$ on the *TiC/SiC* system in a greyscale. In this case the transonic state coincides with the bulk shear wave velocity of SiC. The RSAW of TiC is much more intense than the SW curves.

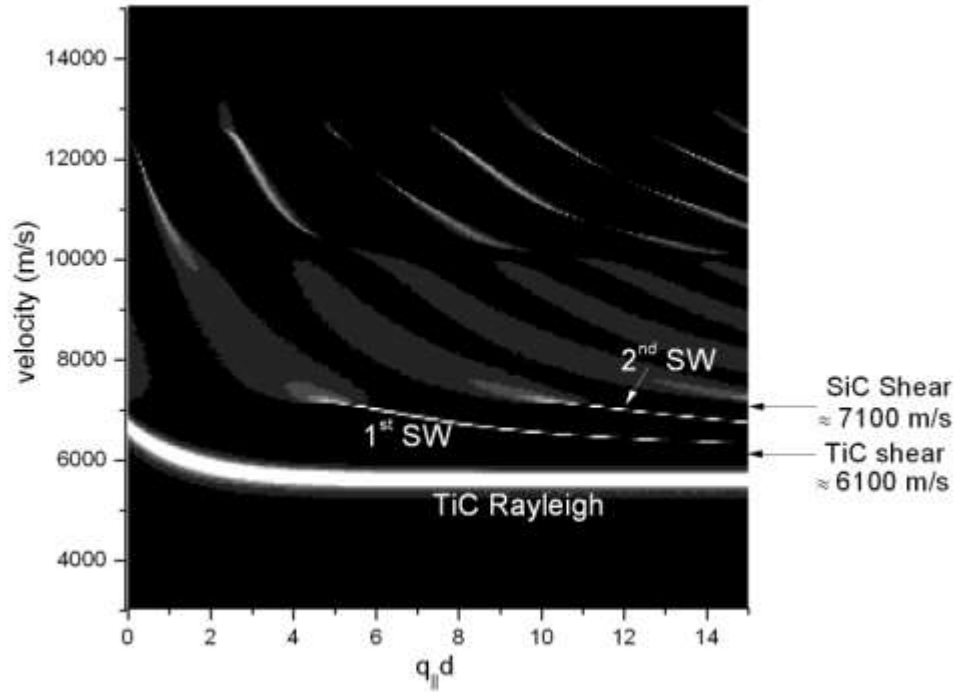


Figure 4.7: Brillouin intensities calculated by the elastodynamic Green's function using the G_{33} component for the *TiC/SiC* system. It shows the dispersion of the RSAW and SW. Broad resonances are clearly recognizable from the broadening of the curves in the supersonic region.

Only two SWs are observed in the region $2 < q_{\parallel}d < 15$ and they lie in the subsonic region. In the supersonic region, only broad resonances are clearly identified as indicated by the wide broadening of curves. Comparison of figure 4.7 and figure 4.5 shows that there are rather few modes in a weak loading system, *TiC/SiC*, compared to a strong loading system, *TiC/diamond*. For the strong loading system, RSAW and SWs in combination with pSWs readily provide sufficient data for the determination of elastic stiffnesses.

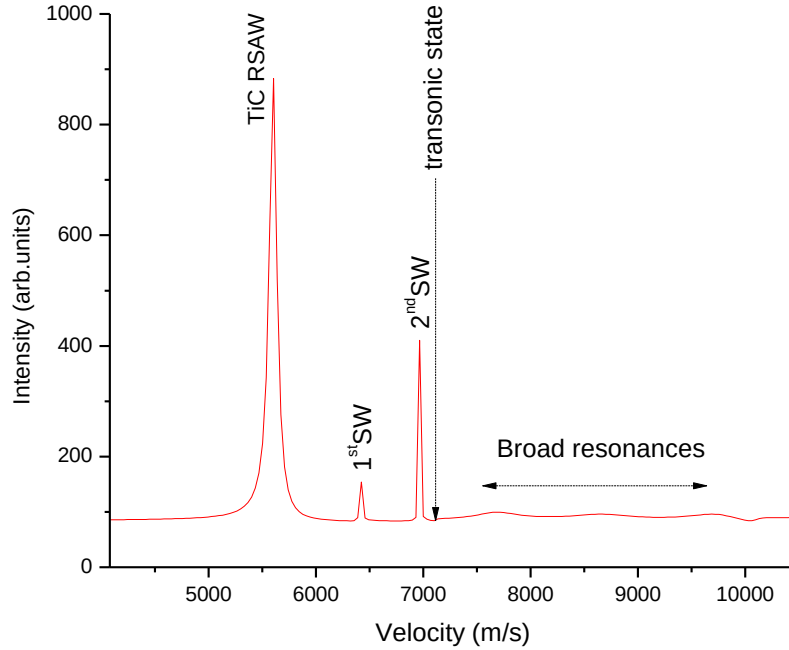


Figure 4.8: Calculated surface-ripple Brillouin spectrum for a 500 nm ($q_{\parallel}d = 11.5$) TiC layer on SiC. SWs are visible in the velocity region between the RSAW and the transonic state. The transonic state coincides with the shear wave velocity of SiC. No pSWs are identified in this system, but broad resonances are clearly visible in the supersonic region.

4.5 Concluding remarks

We have seen that thin supported films can be produced such that one has a fast on slow system or conversely one can have a slow on fast system. Surface Brillouin scattering spectra and dispersion relations have been calculated for both strong and weak stiffening and loading systems using a Green's function method based on a ripple scattering mechanism. It is clear that the elastic moduli and density of both the film and substrate affect the dispersion relation.

Lefevre *et al.*, 1998 developed the theory of wave propagation in stiffening systems where two types of SAW dispersion were revealed, the splitting type and the non-splitting type. The splitting type behaviour arises when the elastic properties of the two materials are quite dissimilar. This behaviour has been categorised in this work as the strong stiffening situation. The second type of behaviour, the non splitting type, arises when the elastic properties of the layer and substrate are not very different. This has been categorised as the weak stiffening situation. Alesksandrov *et al.*, 1994 and Pang *et al.*, 1999 investigated fast on slow systems of CaF_2/GaAs and TiN/HSS , respectively. They both observed a discontinuity in the pSAW at some critical value of $q_{\parallel}d$. The discontinuity is confirmed by our calculations for the strong stiffening situation (splitting type). A pre-Rayleigh mode has also been identified for the strong stiffening situation. However both the discontinuity and the pre-Rayleigh are not observed in a weak stiffening situation (non-splitting).

Previous studies on slow on fast systems (Zhang *et al.*, 1998; Wittkowski *et al.*, 2004; Djemia *et al.*, 2001) reported that, in addition to the RSAW, there exist film guided modes known as SWs whose displacement fields extend throughout the layer and decrease exponential with depth into the substrate. SW-like peaks known as pSW were also reported in some cases. We have seen in our calculations that these pSW are restricted to strong loading systems only.

Given a thin film, a complete set of elastic stiffnesses may be extracted by the simultaneous fitting to the experimental dispersion curves, v vs. $q_{||}d$, for the observed modes (Wittkowski *et al.*, 2006). The best fit is obtained by a least-squares minimization procedure namely

$$\chi^2 = \sum_{SAWs} (v_i^{meas} - v_i^{calc})^2 \quad (4.23)$$

where v_i^{meas} is determined from the SBS spectra and v_i^{calc} is determined by Green's function method.

The experimental studies in the present work were carried out for the weak varieties of both stiffening and loading systems, i.e. *TiC/Si* and *TiC/SiC* systems, respectively. The results are presented in chapter 6.

Chapter 5

Titanium Carbide Thin Film Preparation and Characterisation

5.1 Introduction

Properties of deposited titanium carbide (TiC) films depend strongly on the deposition method and conditions. There are many methods used to deposit TiC films such as chemical vapour deposition (CVD) (Asada *et al.*, 1993; Konyashin, 1996; Guzman *et al.*, 1998; Choy, 2003), pulsed laser deposition (PLD) (Tang *et al.*, 1997; Santerre *et al.*, 1999) and physical vapour deposition (PVD) (Fillity and Perry, 1988; Quinto, 1996; Kusano, *et al.*, 1999). One major advantage of PLD and PVD processes is that compound films can be prepared at low substrate temperatures (Rist and Murray, 1991; Helmersson *et al.*, 2006). This is especially convenient in order to preserve the bulk properties of the substrate during the deposition process. Usually CVD methods are limited owing to high temperatures involved during the process.

PVD processes are divided into evaporation and sputtering. In evaporation, atoms are removed from the source by thermal means, whereas in sputtering, surface atoms are removed from a target material by the interaction of incident particles and ions of a gas. The deposition of thin films by sputtering involves the acceleration of ions in many cases from gaseous (inert gas) plasma to bombard a negatively biased target material. The thin films in the present work were prepared using the sputtering method.

Sputtering was first observed in a dc gas discharge tube by Grove in 1852 (Grove, 1852) and five years later Faraday produced thin films using the evaporation method (Faraday, 1857). Sputtering allows the deposition of thin films with the same composition as the target source. This is the primary reason for its widespread use in the deposition of metal alloy systems (Berry, *et al.*, 1968; Kiyotaka and Hayakawa, 1992; Smith, 1995). The sputtering process can be divided into three categories, namely;

- direct current (DC) sputtering,
- radio frequency (RF) magnetron
- reactive sputtering.

However, there is variance within each category (e.g. DC bias) and hybrids between categories (e.g. reactive RF).

In the present work TiC thin films were synthesized using RF magnetron sputtering and characterized by X-ray reflectometry (XRR), glancing incidence X-

ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) to assess the quality of the films for surface Brillouin scattering (SBS) studies.

5.2 Importance of surface quality

SBS probes surface acoustic excitations in the GHz frequency range. The particle displacement of surface waves decays exponentially beneath the surface, extending on the order of a wavelength into the bulk. The elastic properties studied by SBS are therefore associated with the region within a few hundred nanometres of the surface and can differ with those of the bulk. There are a number of reasons attributed to these variations. Among which includes the near surface damage caused by polishing or ion bombardment, surface roughness or impurities in the form of surface films.

5.2.1 Surface damage due to polishing

Mendik *et al.*, (1992) showed that the surface damage caused by polishing a nickel single crystal resulted in lower measured surface acoustic wave (SAW) velocity as compared to theoretical values. There was a roughly 6% decrease of the measured SAW velocities as compared to those calculated from bulk elastic constants. However scanning acoustic microscopy (SAM), which probes much greater depth than SBS, gave velocities comparable to the calculated values. To improve the SBS results, the samples were sputtered and annealed so as to reduce the amount of

surface damage. They reported a 3% increase in the SBS velocities, while the SAM results showed hardly any change.

5.2.2 Surface roughness

It is found that the surface roughness of samples is crucial for the successful measurement of surface acoustic modes. Smooth or polished surfaces produce less elastic scattering of light and thereby enhance the detection of weak inelastic scattering peaks in the Brillouin spectrum. Eguiluz and Maradudin (1983) showed theoretically that surface roughness not only attenuates surface waves but also decreases their frequency $\omega(q_{\parallel}) = vq_{\parallel}$, where $q_{\parallel}$ is defined in Chapter 2 as the surface wave vector component parallel to the surface and v is the velocity. The shift in frequency $\omega_i(q_{\parallel})$ can be written conveniently in the form

$$\frac{\omega_i(q_{\parallel})}{\omega(q_{\parallel})} = (\delta/\tau)^2 \omega_i(\tau q_{\parallel}), \quad (5.01)$$

where δ is the root mean square (roughness) departure of the surface from flatness and τ is the average distance between peaks and valleys in the rough-surface profile. In Eq. (5.01) it is seen that the ratio of the frequency shift $\omega_i(q_{\parallel})$ and the frequency $\omega(q_{\parallel})$ of a Rayleigh wave propagating on a flat surface is given by the product of the "universal" function $\omega_i(\tau q_{\parallel})$ and the $(\delta/\tau)^2$ ratio which describes the rough-surface profile. The "universal" function $\omega_i(\tau q_{\parallel})$ relates the frequency shift of a surface wave to the scale of the surface roughness. Figure 5.1 shows the frequency shift of a Rayleigh wave due to surface roughness as a function of the product $\tau q_{\parallel}$.

In summary, any imperfections on the surface region e.g., dislocations, pores and micro cracks contribute to a decrease in SAW velocities measured by SBS and an increase in the elastically scattered light. In the present work, no polishing of the film surface was necessary as very smooth surfaces were produced. The roughness of the films were measured by the XRR technique as discussed in Section 5.4.2.

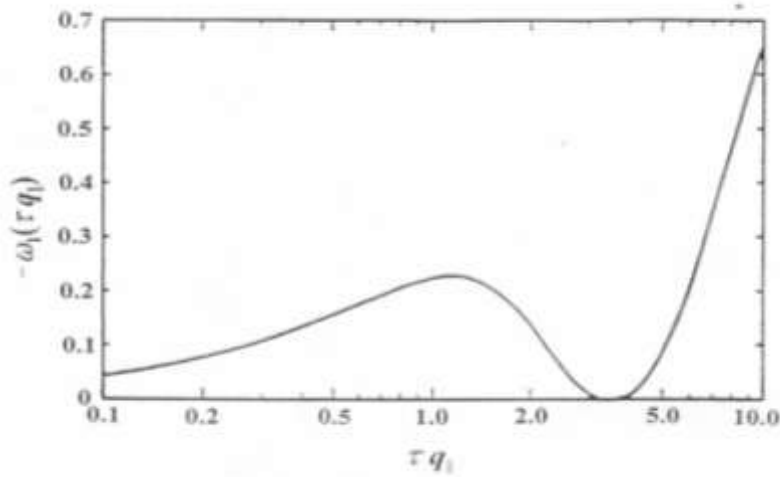


Figure 5.1: Rayleigh frequency shift due to surface roughness as a function of $\tau q_{\parallel}$ (After Eguluz and Maradudin, 1983).

5.2.3 Impurities in the form of surface films

A native oxide layer on the surface of a film or substrate will inevitably shift the frequency of the SAW. If we take silicon as an example, it is known that commercial silicon supports a native oxide layer of about 2 nm thick. Hence this will have an effect on the measured SAW velocity. In the case of substrates, a useful practice is to sputter etch the substrates prior to deposition so as to remove the oxide layer. However, little can be done if the material deposited has a high affinity for

oxygen. The substrates used in the present work were sputter etched for 5 minutes prior to deposition.

5.3 Film preparation

5.3.1 RF magnetron sputtering

Magnetron sputtering can be done in either DC or RF modes. In RF magnetron sputtering, a radio frequency (RF) signal superimposed on a target self-bias (usually negative) is used to ionize the inert gas. This will generate a self sustained glow discharge constituting mainly of positive gas (argon) ions. The schematic diagram of the entire sputtering process is shown in figure 5.2. The magnets located behind the targets are used to increase the percentage of electrons that take part in ionisation events. This will increase both the probability of electrons striking the argon atoms and the length of electron path and hence increase the ionisation efficiency significantly. The negative potential difference between the target (biased negatively) and the plasma, extracts Ar^{2+} ions from the plasma and accelerates them onto the target. The surface atoms of the target are ejected by momentum transfer and are deposited as thin films into the surface of the substrate. Sputter yield, S , is defined as the mean number of atoms removed from the surface of solid per incident ion. The sputter yield is a process parameter that is influenced by the RF power, gas pressure and target material.

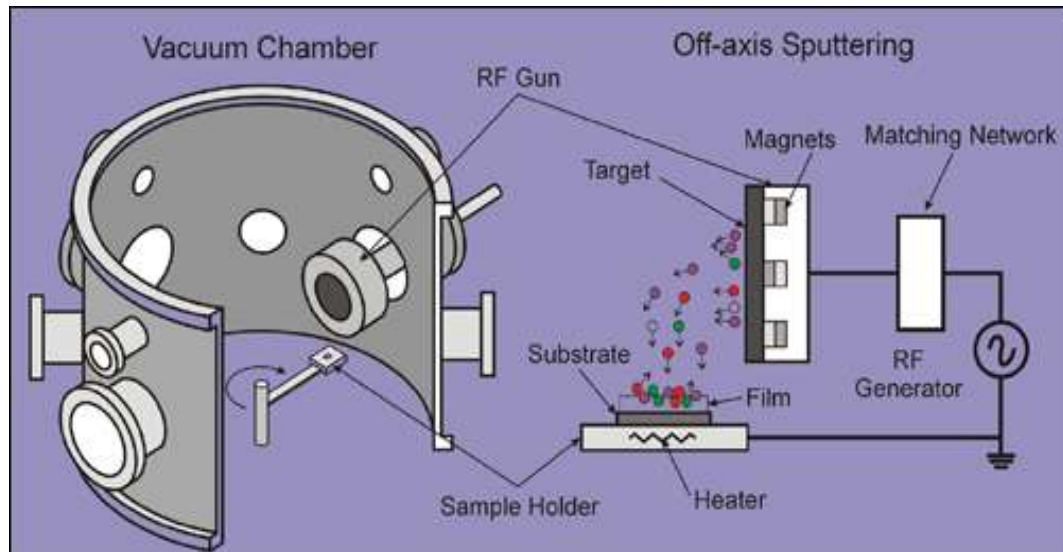


Figure 5.2: Schematic diagram of RF sputter system with the sputtering process shown adjacent thereto (after www.phasis.ch).

Sputtering has no limitation regarding target materials and both pure metals and insulators can be grown as deposited films. For insulators an RF power supply is needed in order to avoid charge build-up on the target surface (Ohring, 1992). The presence of a matching network between the RF generator and the target is necessary in order to optimize the power dissipation in the discharge.

5.3.2 Experimental procedure

TiC films, on both (100) single crystal silicon ($\approx 15 \times 15 \times 0.5 \text{ mm}^3$) and 6H (0001) silicon carbide ($\approx 4 \times 4 \times 1 \text{ mm}^3$) substrates, with various thicknesses were deposited using the RF magnetron sputtering apparatus in the School of Physics of the University of the Witwatersrand, Johannesburg. Figure 5.3 shows a picture of the

growth chamber and related instruments used in the TiC film deposition. All substrates were ultrasonically cleaned with methanol prior to being loaded into the deposition chamber. The system was evacuated with a fore- and turbo-pump to a base pressure of around 10^{-6} mbar prior to thin film deposition. Such a high vacuum was essential to prohibit target poisoning or contamination or formation of an N_2 / O_2 monolayer during deposition.

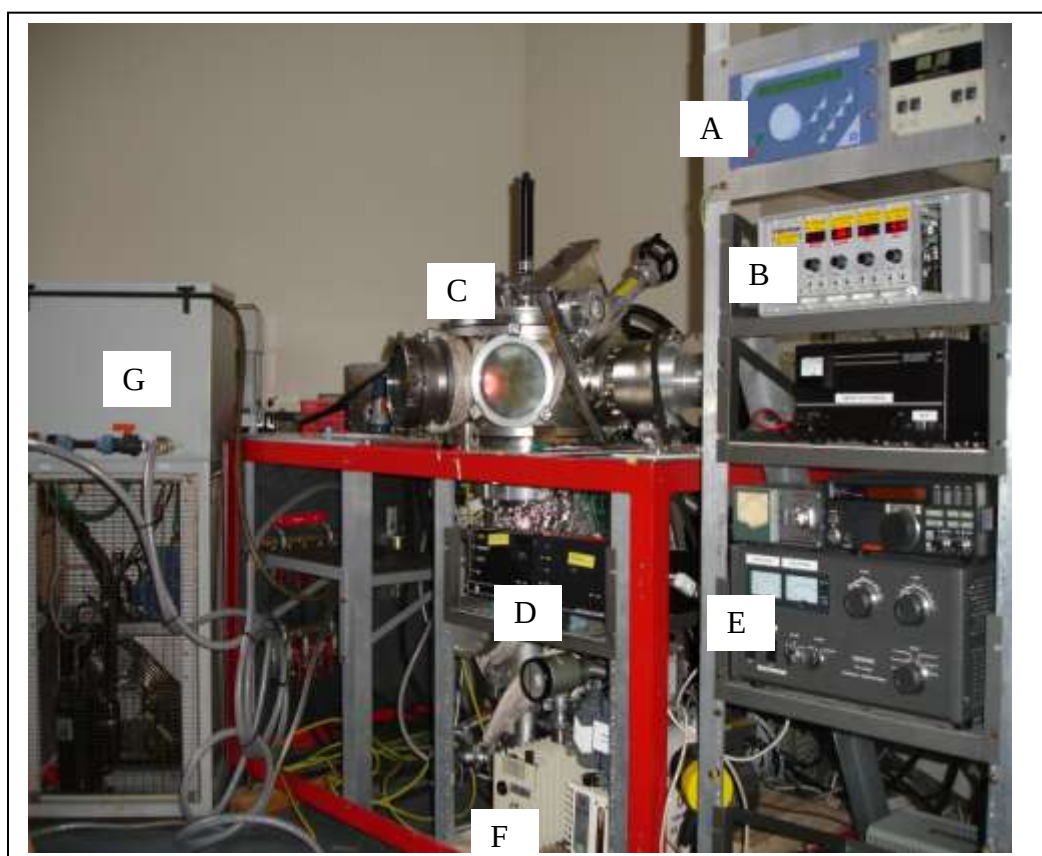


Figure 5.3: RF magnetron sputtering equipment and the related instruments. A– RF generator, PFG 300RF; B – gas control unit; C – vacuum chamber; D – turbo pump control unit, Turbotronik NT 150/360 VH; E – linear amplifier, Kenwood TL-922; F – fore pump; G – Compact cooling unit.

A water-cooled stoichiometric titanium carbide target was used for the deposition of TiC on to a substrate located at 60 mm from the target. The purity grades of the materials involved were 99.9 wt.% for titanium carbide and 99.997 vol.% for argon. The target was sputter-cleaned prior to each deposition for 5 minutes at a power of 250 W. The silicon substrates were etched with very low energy (40 W) for 5 minutes in Ar prior to deposition in order to remove the native oxide layer from the substrate surface. All the films characterized in this work were prepared under similar conditions at an Ar working gas pressure of 6×10^{-3} mbar. A specially designed substrate holder was used for silicon carbide substrates due to their small size ($\approx 4 \times 4 \times 1$ mm³). The substrate holder carries up to 7 substrates and it is equipped with a shutter system to ensure single substrate exposure to the target and plasma during deposition. The thickest intended film layer is deposited first over the entire surface followed by appropriate movement of the shutter to the next substrate. This procedure is continued in an undisturbed manner for each of the 7 films with various thicknesses ranging from 50 nm to 800 nm which were used for SBS measurements.

5.4 Film characterisation

5.4.1 Film thickness

Film thickness is a critical parameter that must be determined accurately in order to obtain dispersion relations for diverse thin film - substrate configurations (such as,

the TiC/Si or TiC/SiC combination) investigated in the present work. For film thickness and deposition rate measurements, two sets of TiC films on silicon were prepared using RF magnetron sputtering. Each set comprised of five thin films prepared at powers of 50W, 100W, 150W, 200W, and 250W. The substrates ($\approx 15 \times 15 \times 0.5$ mm³) from each set were cut from a separate silicon wafer (diameter ≈ 75 mm) and ultrasonically cleaned for each deposition run. To obtain the film thickness, two parallel lines were marked closely to each other at the centre of the substrates using a sharp non-permanent marker. The region covered by the ink provided weak adhesion to the film and could be removed using any organic solvent. All depositions were carried out for 60 minutes to allow sufficient deposition at low powers. After the deposition, the films were immersed in alcohol/acetone to etch away the masked portions of the thin film thereby yield a doubly step edged thin film at the centre of the substrate (Fig. 5.4). Two step edges were preferred to define unambiguous baseline for accurate film thickness determination using a surface profilometry. A profilometer (Dectak Alphastep 5000 provided by DENEL dynamics) was used to scan the step for film thickness determination due to the following reasons:

- a high lateral resolution extending up to 5 mm,
- a high accuracy and precision especially for thin films with thickness > 100 nm.

Figure 5.5 below shows a typical layer thickness measurement for a TiC layer on (100) Si prepared at 200 W.

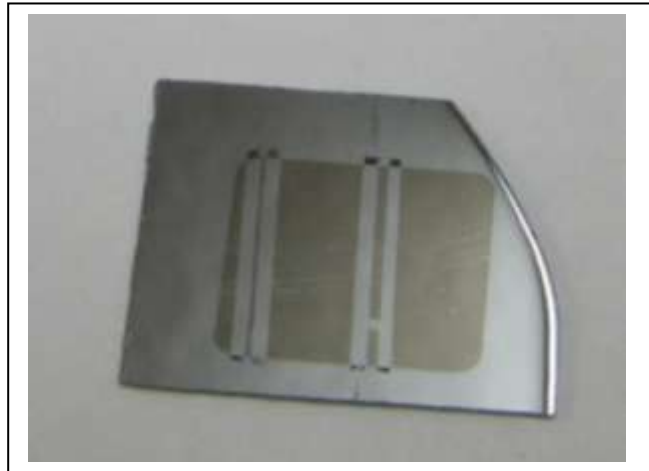


Figure 5.4: A sample of TiC thin film on silicon substrate after immersion in alcohol, showing clearly the two step edges.

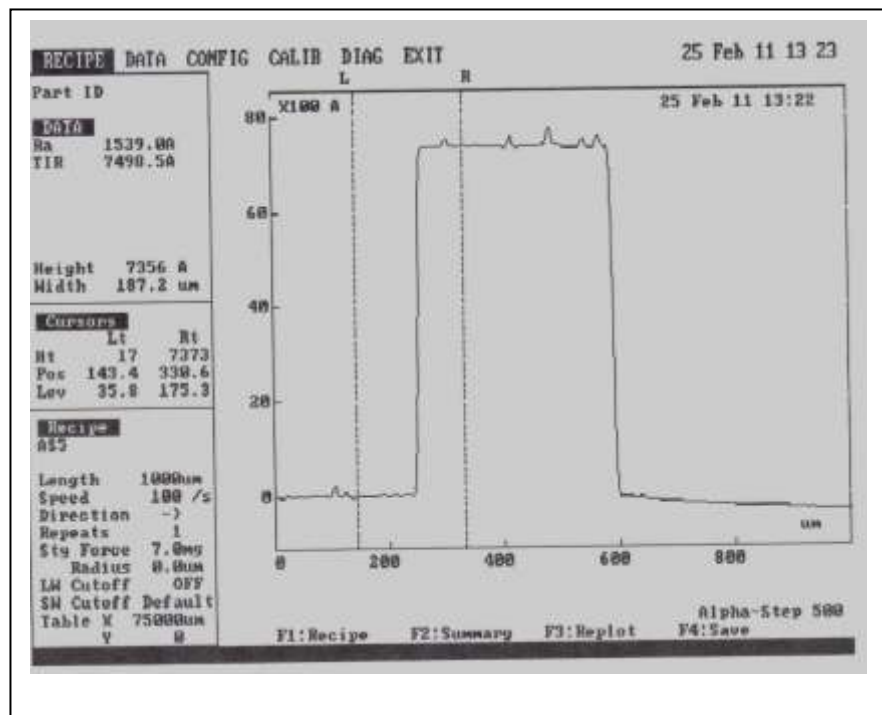


Figure 5.5: Profilometer measurement for a film prepared at 200 W showing a layer thickness measurement of 736 nm.

Table 5.1: Power vs layer thickness measurements for TiC layer on silicon system

Power (W)	Set A Thickness (nm)	Set B Thickness (nm)	% Deviation
50	92	100	-8.7
100	327	320	2.1
150	543	537	1.1
200	731	736	-0.7
250	805	801	0.5

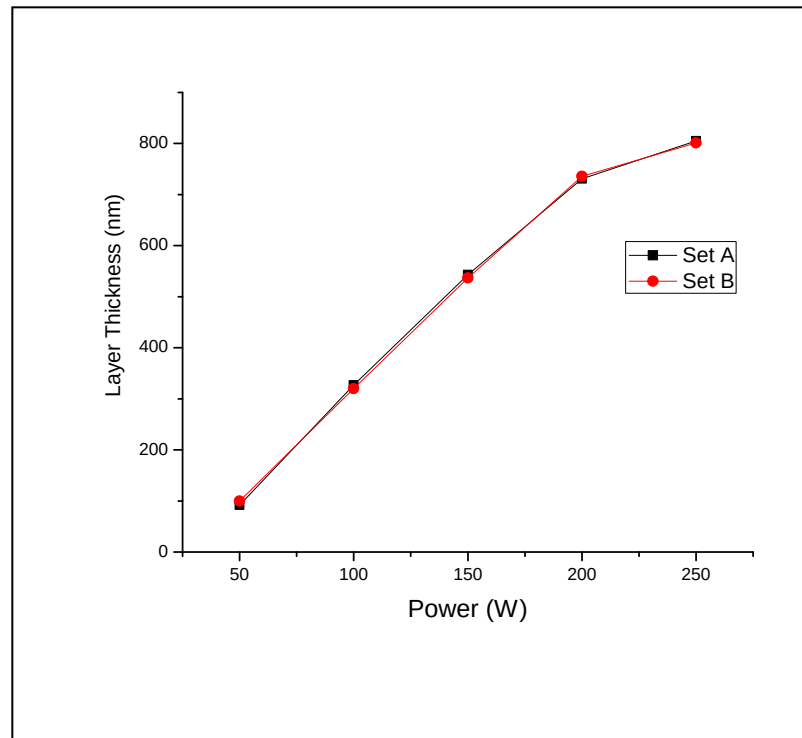


Figure 5.6: Graph of layer thickness against power. Points are joined as a guide to the eye, not as the best fit.

From Table 5.1 and figure 5.6 it can be concluded that there is a linear relationship between the layer thickness and applied power up to 200 W. The deposition rates for different powers are deduced from Table 5.1 by taking the average of Set A and Set B and are presented in Table 5.2.

Table 5.2: Deposition rates at different powers for TiC films

Power (W)	50	100	150	200	250
Average thickness (nm)	96.0	323.5	540.0	733.5	803.0
Deposition Rate (nm min⁻¹)	1.6	5.4	9.0	12.2	13.4

Since ion bombardment energy strongly depends on RF power and the sputtering yield is proportional to the ion bombardment energy, it follows that the sputter rate must strongly depend on the RF power. Table 5.2 confirms that the sputter rate increases with increasing RF power. From these measurements, it was decided to use a power of 200 W (the highest giving linear deposition rate). This power corresponds to a deposition rate of 12.2 nm min⁻¹. The behaviour of the deposition rate beyond 200 W was not established since 250 W was the maximum power which could be used with the available RF generator.

5.4.2 X-Ray reflectometry (XRR)

XRR is a non-destructive and non-contact technique used for the determination of thickness, density and roughness of films with high precision. The technique

involves monitoring the intensity of the X-ray beam reflected by the specimen at grazing angles usually less than 5° in the incident angle. A thorough description of XRR can be found elsewhere (Holý *et al.*, 1998; Bontempi *et al.*, 2000; Schug *et al.*, 2001; Kohli *et al.*, 2001).

In principle a monochromatic X-ray beam of wavelength λ irradiates a sample at a grazing angle θ_R and the intensity reflected at an angle $2\theta_R$ is recorded by a detector. Total reflection will occur at or below a certain angle, θ_c – the critical angle. The angle varies depending upon the electronic density of the material. For ideal flat surface the reflectivity decreases at angles above the critical angle in proportion to θ_R^{-4} . If the material surface is rough, a more drastic decrease in reflectivity occurs. This is because roughness gives rise to diffuse scattering, resulting in less intensity in the specularly reflected beam. Given a thin film evenly overlaid on the substrate with electronic density different from the substrate, the reflected X-rays from the interface between the substrate and the thin film as well as from the free surface of the thin film will interfere constructively and destructively. The period of the interference fringes and the fall in the intensity are related to the thickness and the roughness of the layer. As a result density (ρ), film thickness (d), and roughness (σ *rms*) may be extracted from the critical angle, interference spectra, and reflectivity.

The following discussion follows closely the treatment of Bontempi *et al.*, 2000. At X-ray frequencies, the refractive index, n , can be expressed as

$$n = 1 - \delta - i\beta, \quad (5.02)$$

where

$$\delta = \frac{\rho_e r_e \lambda^2}{2\pi}, \quad (5.03)$$

$$\beta = \frac{\mu \lambda}{4\pi}, \quad (5.04)$$

ρ_e is the electron density, r_e is the classical electron radius $= e^2 / mc^2$, λ is the X-ray wavelength and μ is the linear absorption coefficient for energies far from X-ray threshold. From the measurement of the critical angle, the density of the film can be estimated by the formula

$$\theta_c = \sqrt{2\delta} = \lambda \sqrt{\frac{r_e \rho_e}{\pi}}. \quad (5.05)$$

For incident angles greater than θ_c ($\theta_R > \theta_c$) the X-ray beam penetrates inside the film. Reflection will therefore occur at the top and bottom surfaces of the film. The interference between the rays reflected from the top and the bottom of the film surfaces results in interference fringes. For intensity maxima, the path difference between the reflected waves should be an integral multiple of the incident wavelength,

$$m\lambda \approx 2d\sqrt{\sin^2 \theta_m - \sin^2 \theta_c}, \quad (5.06)$$

where m is an integer. Since the angles are small, equation (5.06) can be expressed as

$$m\lambda \approx 2d\sqrt{\theta_m^2 - \theta_c^2}. \quad (5.07)$$

The layer thickness is therefore given by

$$d = \frac{1}{2} m\lambda \frac{1}{\sqrt{\theta_m^2 - \theta_c^2}}. \quad (5.08)$$

For very small angles ($\theta_r < 0.2^\circ$), the scattered X-ray intensity is almost constant, whereas above the critical angle the intensity rapidly drops by several orders of magnitude and oscillations appear in the spectrum. These oscillations are called Kiessig fringes (Bontempi *et al.*, 2000). The presence of surface roughness decreases the specular intensity of the whole curve progressively and interface roughness gives rise to progressive damping of the Kiessig fringes.

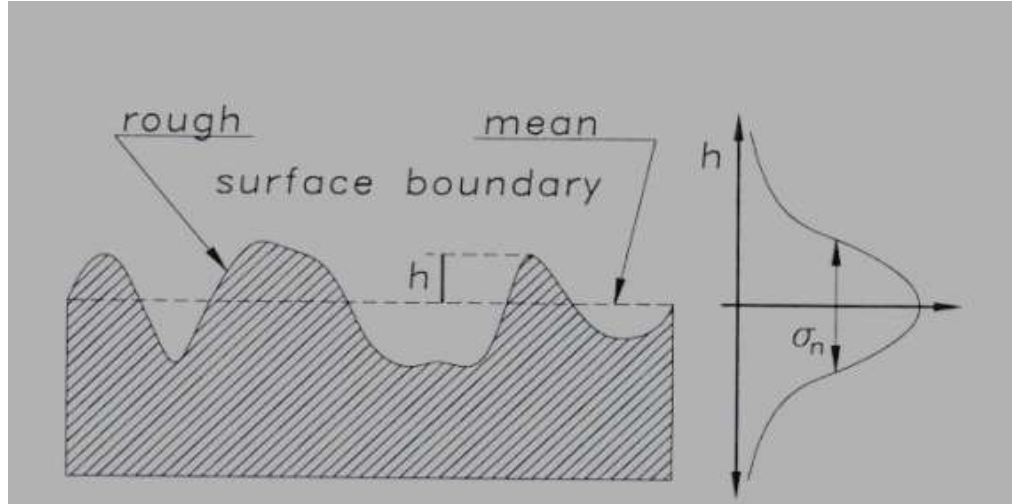


Figure 5.7: Interface roughness according Névot and Croce, 1980. The roughness of the interface is described using the Gaussian function (*after Filies et al.*, 1999).

Surface or interface roughness can be obtained, by a refinement of the experimental data with algorithms put forward by Névot and Croce, 1980. They considered roughness by assuming non-homogeneous thickness. They assumed that the rough interface may be estimated by a Gaussian distribution of peaks and valleys with a mean d (layer thickness) and a standard deviation σ_n (Fig. 5.7). Thus, the roughness coefficient may be calculated (Filies *et al.*, 1999) as

$$\zeta_n = \exp\left(-8 \frac{\sigma_n^2}{\lambda^2} f_n f_{n-1}\right), \quad (5.09)$$

where f_n are the Fresnel factors for the n th interface.

The XRR method gives accurate measurements for layer thicknesses, d , of less than 200 nm (Wamwangi, 2012). Three samples of TiC films ($d \leq 200$ nm) on Si(100) substrates were prepared using RF magnetron sputtering at 100 W, 200 W and 250 W for 28 min, 14 min and 13 min, respectively for XRR measurements. The corresponding layer thicknesses of 151.2 nm, 170.8 nm and 174.2 nm, respectively, were extracted from the deposition rates of Table 5.2.

A Bruker New D8 Discover X-ray diffractometer was used for all the XRR measurements in the present work. Figures 5.8 and 5.9 show XRR results for films deposited using RF magnetron sputtering at 100 W and 200 W, respectively.

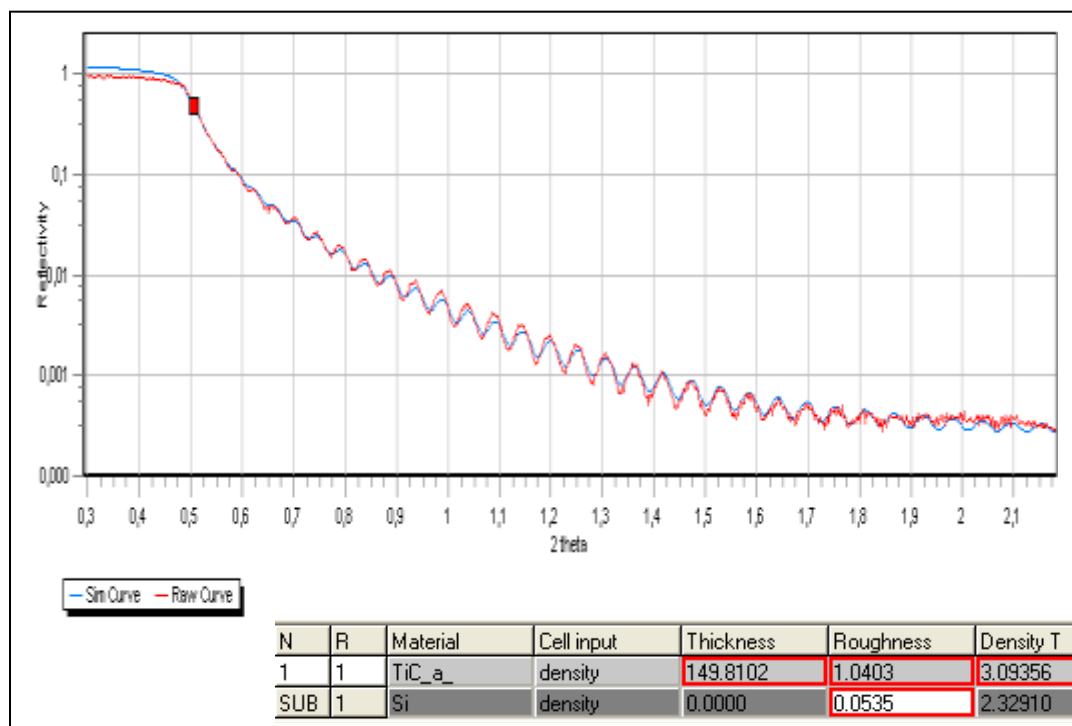


Figure 5.8: XRR measurement for a TiC film on silicon prepared at 100 W for 28 min. The fit parameters for the simulation curve are highlighted in red. The parameter values are: layer thickness 149.81 nm, roughness 1.04 Å and density 3.09 g/cm³

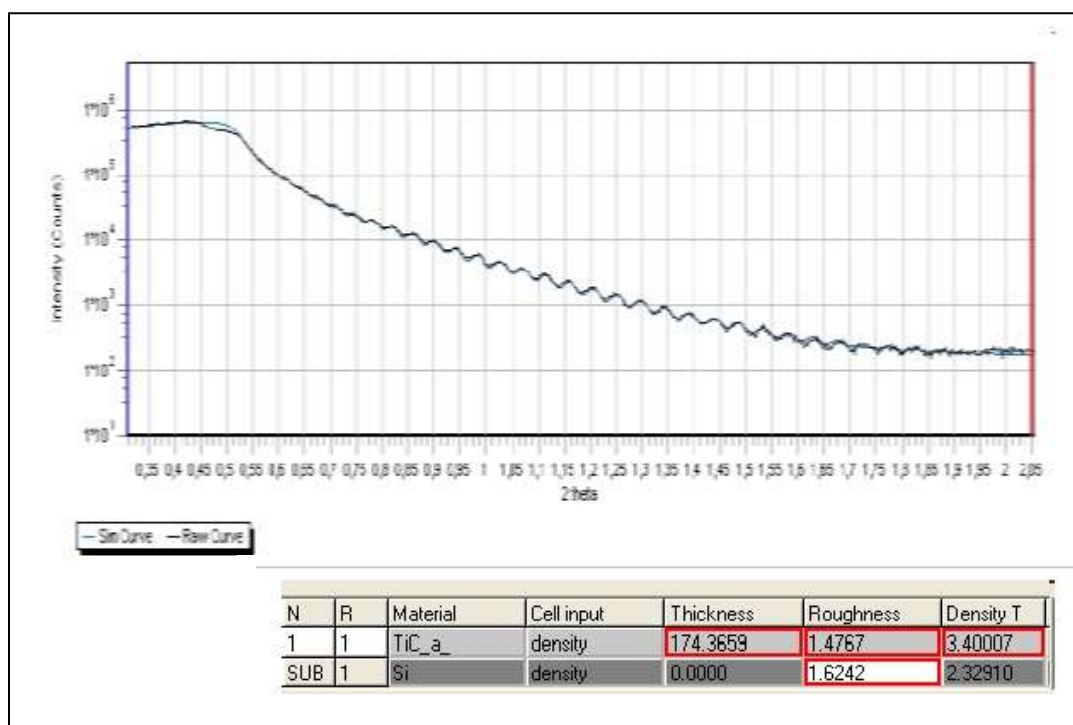


Figure 5.9: XRR measurement for a TiC film on silicon prepared at 200 W for 14 min. In this figure the y-axis is given as intensity in arbitrary units instead of the normalised reflectivity. The fit parameters for the simulation curve are highlighted in red. The parameter values are; layer thickness 174.37 nm, roughness 1.48 Å and density 3.40 g/cm³.

Table 5.3: XRR results for TiC films prepared at 100 W, 200 W and 250 W

Power (W)	Density (g/cm³)	Roughness (Å)	XRR Thickness values (nm)	Profilometer Thickness values (nm)	Deviation
100	3.09	1.04	150	151	-1%
200	3.40	1.48	174	171	2%
250	3.63	0.72	172	174	-1%

There is a steady increase in the density of the films with increase in the RF power but it remains less than that of bulk TiC, which is 4.9 g/cm³ (Petersen, 1982). The increase in film density is attributed to increase in adatom surface energy with RF sputter power which enhances thin film compactness. The roughness of the films remains low regardless of the RF power and the layer thickness values are in good agreement with values measured using the profilometer. Density and layer thickness values are useful in the calculation of theoretical SBS spectra as outlined in Chapter 2. Low roughness values imply that less elastic light will be observed in SBS measurements. This will enhance the detection of weak inelastic scattering peaks.

5.4.3 Glancing incidence X-ray diffraction (GIXRD)

In a GIXRD experiment, an X-ray beam is directed onto the surface of the film at an incident angle (α_d) of 1° or less and the detector is placed in a horizontal plane, parallel to the film surface to record diffraction from lattice planes which are

perpendicular to the surface (Fig. 5.10). Radial ($2\theta_d$) scan and/or angular (ω) scan methods can be used to collect GIXRD data. In a radial scan, both the film and the detector are scanned to record diffraction along a fixed direction on the substrate while in an angular scan the detector is stationary at a fixed $2\theta_d$ angle, while the film rotates about its surface normal to record in-plane diffraction from lattice planes which have fixed lattice spacing (Agarwal 1979; Segmüller 1991).

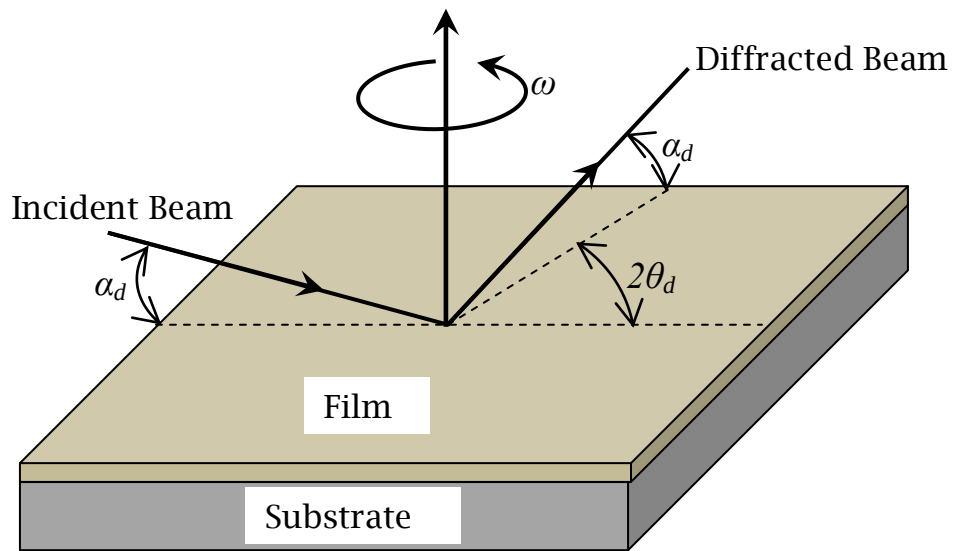


Figure 5.10: Schematic diagram of the GIXRD geometry.

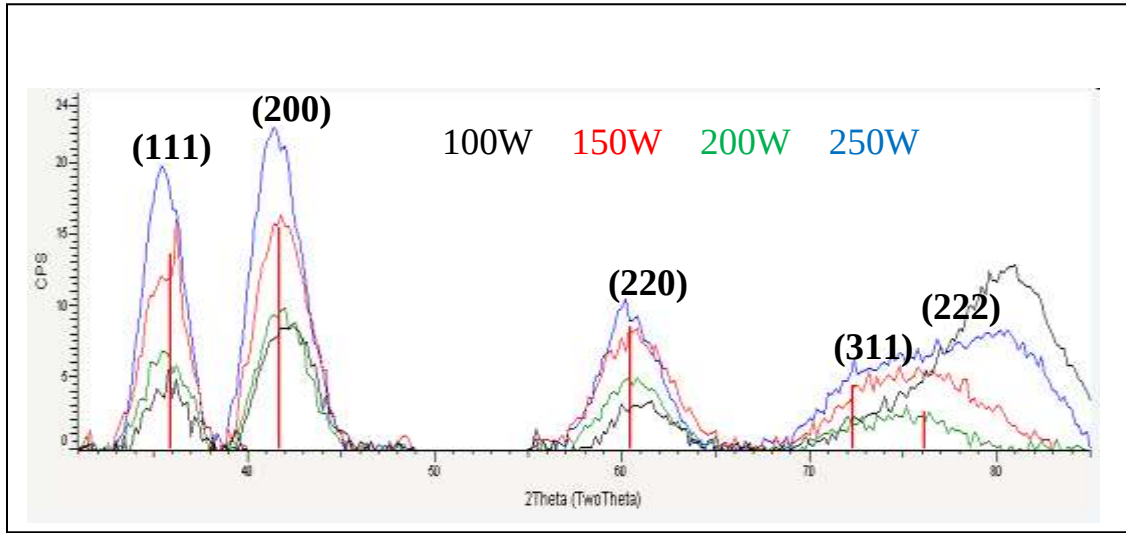


Figure 5.11: GIXRD measurements for TiC films prepared at 100 W, 150 W, 200 W and 250 W.

TiC films of 180 nm layer thickness were grown by RF magnetron sputtering on (001) silicon substrates, for this measurement. The films were prepared at 100 W, 150 W, 200 W and 250 W. A Bruker D8 Advance reflectometer equipped with a Göbel mirror was used for the measurements. A Göbel mirror comprises parabolically bent multilayers with a laterally graded period to achieve monochromatic and parallel X-ray beams (Kohli *et al.*, 2002; Schuster and Göbel, 1995).

The measurements were taken using a radial scan. The data were used to determine the orientation and crystallite size of the films. The incidence angle, α_d , was kept at a low value of 0.75° in order to maximize the signals from the layers and

minimize the substrate reflections. The measurements were performed for a $2\theta_d$ range of 30° to 90° . The measurements show that there is no preferential orientation for all samples. There is however a random distribution of crystallites. The identification of the (111), (200), (220) reflections (Fig. 5.11) is clearly attributive of the cubic TiC structure but their low intensities indicate an amorphous structure with randomly distributed crystallite grains. The peak at 80° for the 100 W and 250 W samples is not so clearly identified. From the identified peaks, the crystallite size can be roughly estimated to be 3 nm using the Scherrer equation (Cullity, 1978) for all samples.

5.4.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) can be used to determine the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a film. In order to verify the stoichiometry of TiC films, two samples of *TiC/Si* were analysed using XPS equipment (PHI 5000 Versaprobe – Scanning ESCA Microprobe) at the University of the Free State, South Africa. The two films of 488 nm and 732 nm thicknesses were deposited at 200 W. Figure 5.12 shows a typical XPS raster spectrum of the deposited TiC films. Ti, C, O, N and Ar-related peaks were clearly identified. From this survey spectrum, regions of interest were identified and high resolution C 1s, Ti 2p and O 1s XPS peaks were recorded.

Figures 5.12, 5.13 and 5.14 shows the XPS survey spectra for a 488 nm TiC film deposited on silicon showing clearly the C 1s, Ti 2p and O 1s peaks. Table 5.4 summarizes the assignments of the peaks with binding energies.

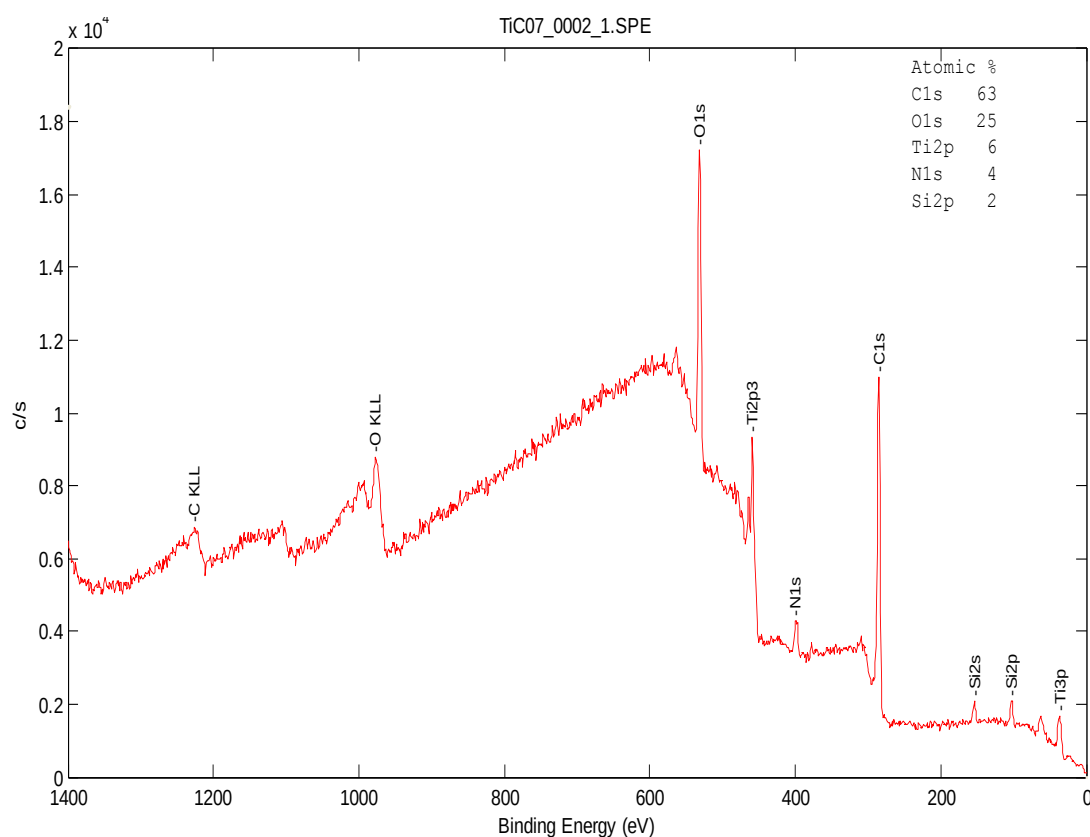


Figure 5.12: XPS survey on the unetched surface of a 488 nm TiC film deposited on silicon at 200 W. The atomic percentage of the elements at the surface are 63% C 1s, 25% O 1s, 6% Ti 2p, 4% N 1s and 2% for Si 2p.

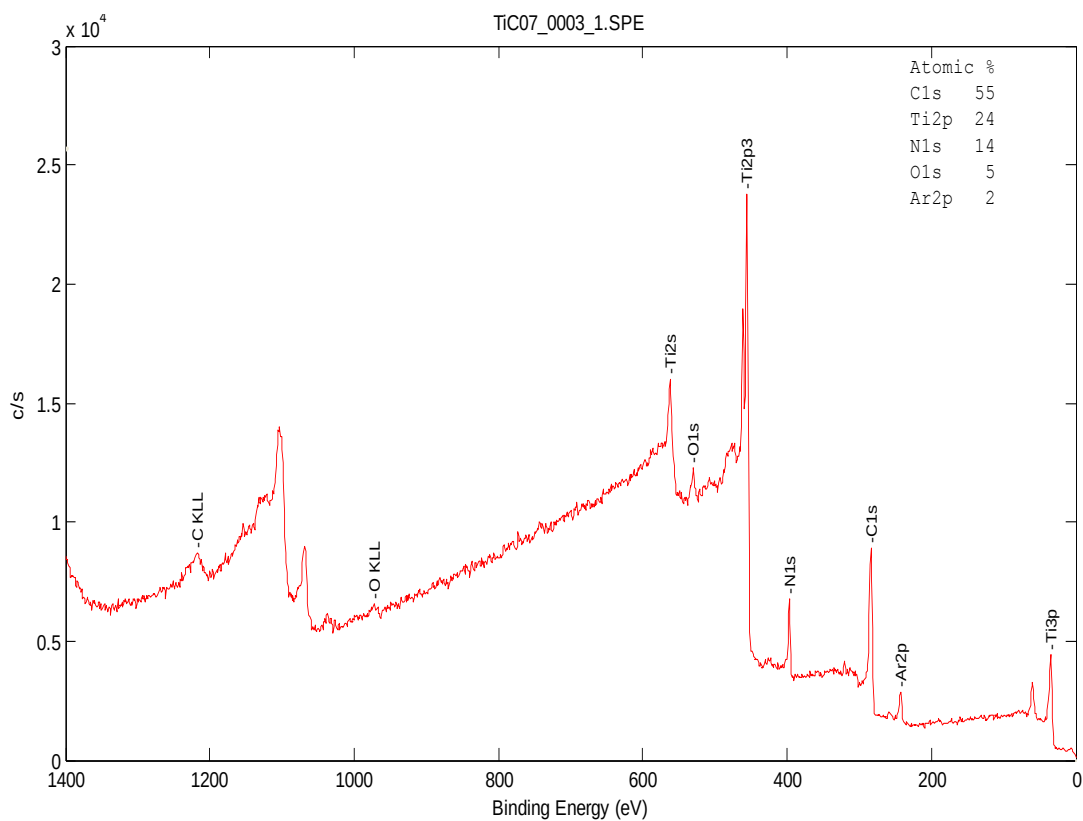


Figure 5.13: XPS survey spectrum of a 488 nm TiC film deposited on silicon at 200 W. This was obtained after sputter etching for 1 min. The atomic percentage of the elements are 55% C 1s, 24% Ti 2p, 14% N 1s, 5% O 1s, and 2% for Ar 2p.

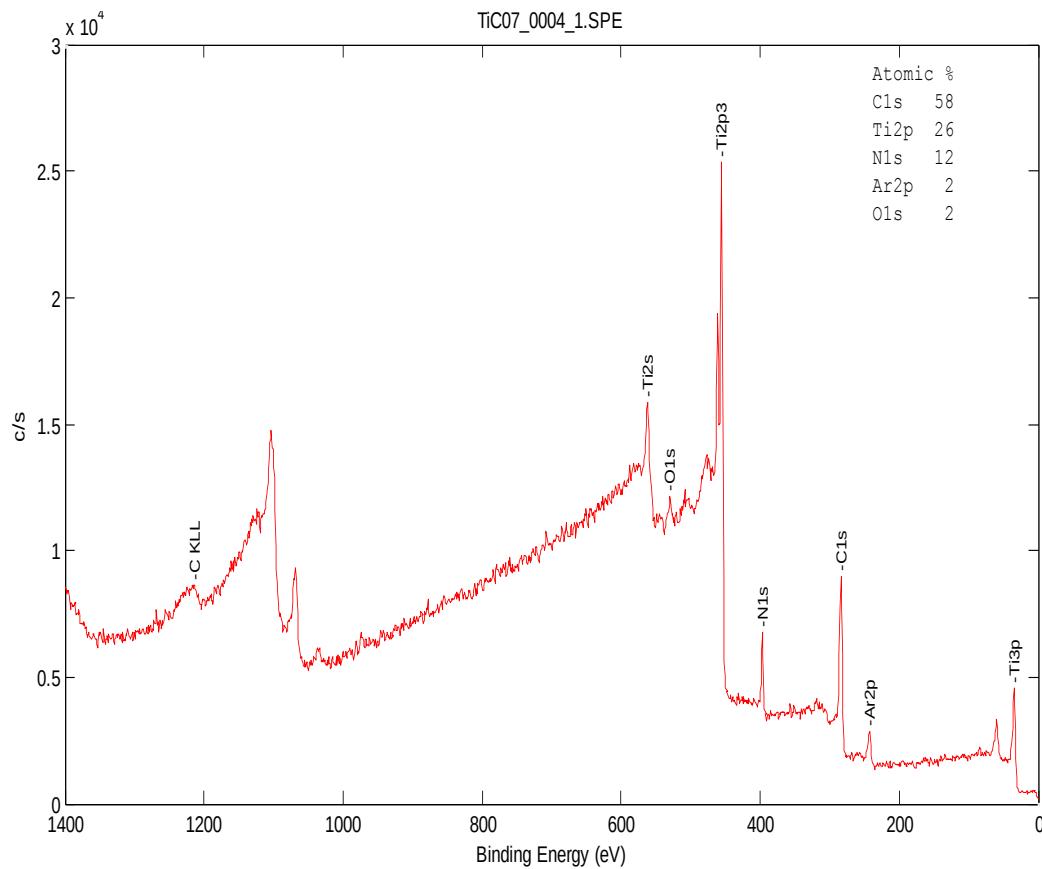


Figure 5.14: XPS survey spectrum of a 488 nm TiC film deposited on silicon at 200 W. This was obtained after sputter etching for 2 min. The atomic percentage of the elements are 58% C 1s, 26% Ti 2p, 12% N 1s, 2% O 1s, and 2% for Ar 2p.

XPS surveys were done with a 100 μm Al monochromatic X-ray beam at a power of 25 W and voltage of 15 kV. As for depth profiling, a 2×2 mm raster Ar ion gun was used at 2 kV with a current of 2 μA . The sputter rate was about 85 $\text{\AA}/\text{min}$. The XPS survey on the surface (Fig. 5.12) shows a very strong oxygen signal (25% atomic percentage). This is reduced to 5% (Fig. 5.13) after etching for 1 min and further reduced to 2% (Fig. 5.14) after etching for 2 min (≈ 170 $\text{\AA}$ deep). This shows that oxygen is predominantly at the surface of the films extending to a thickness of about 170 $\text{\AA}$. There is however evidence that nitrogen is incorporating itself in the film as evident from a constant atomic percentage of 12% regardless of etching. All the films were prepared in an Ar pressure of 6×10^{-3} mbar, which explains the Ar peak. Other notable elements from the survey are C 1s and Ti 2p. High resolution spectra C 1s, Ti 2p, O 1s and N 1s are shown in figure 5.15. The analysis of the results was done by Prof H C Swart and his group at the University of Free State, South Africa. The results are tabulated in Table 5.4.

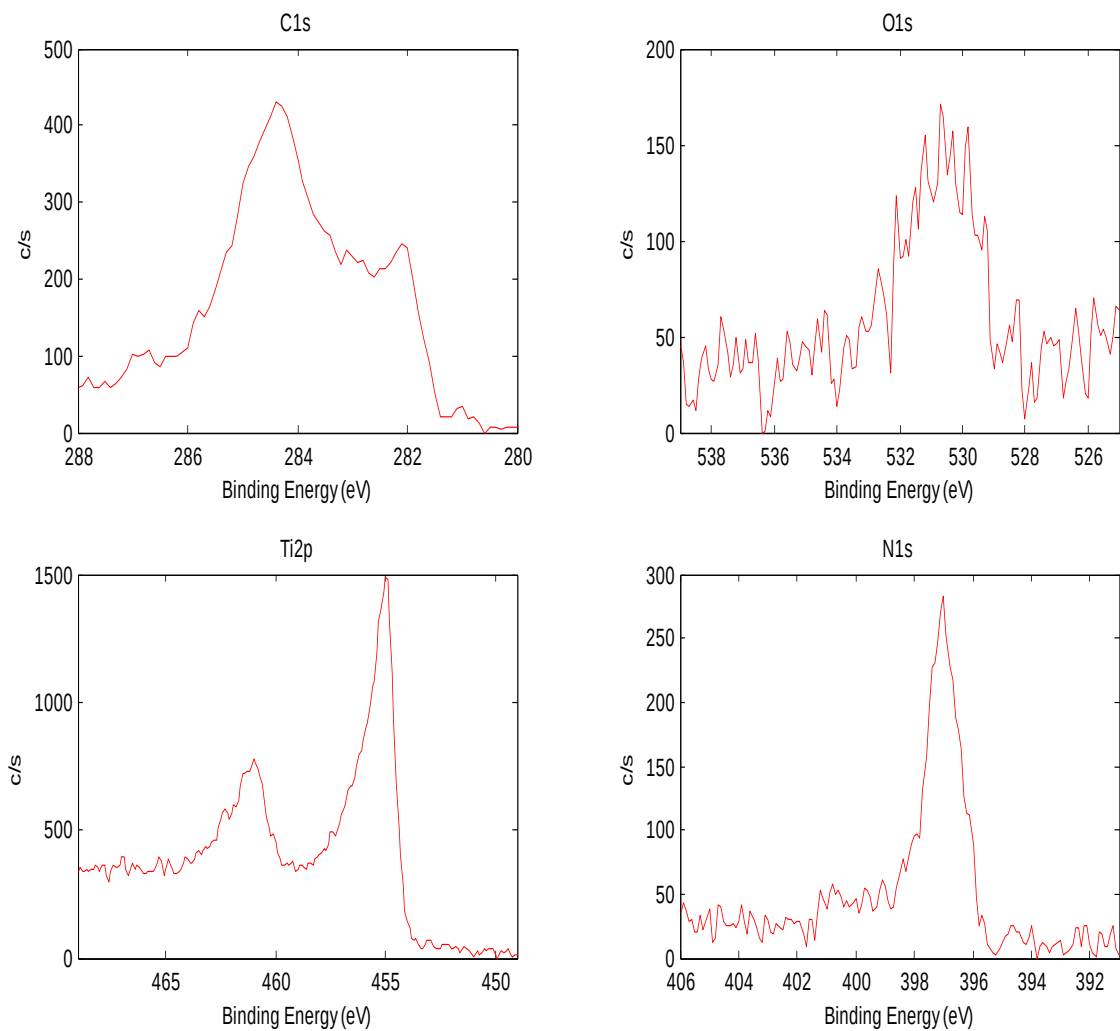


Figure 5.15: Magnified XPS spectra of C 1s, O 1s, Ti 2p and N 1s XPS spectra for a 488 nm TiC film.

Table 5.4: Deconvolution of C 1s, O 1s, Ti 2p and N 1s peaks (Moulder, 1995) for the 488nm TiC film

Peak Position (eV)	Description
<i>(a) Deconvolution of the C 1s peak</i>	
282.5	TiC
284.3	C
285.4	C with N/C with O
<i>(b) Deconvolution of the O 1s peak</i>	
529.7	?/TiO ₂ /TiO
530.8	TiO
532.1	?
<i>(c) Deconvolution of the Ti 2p peak</i>	
455.1	TiC 2p _{3/2}
455.2	TiO 2p _{3/2}
458.4	TiO ₂ 2p _{3/2}
461.2	TiC 2p _{1/2}
461.4	TiO 2p _{1/2}
464.6	TiO ₂ 2p _{1/2}
<i>(d) Deconvolution of the N 1s peak</i>	
397	?TiN
399	?N with C/C ₅ H ₅ N

From the high resolution XPS spectra of the peaks (Fig. 5.15), it can be inferred that two major chemical compounds are present: the isolated carbon is represented by C 1s peak of 284.3 eV and TiC is represented by three peaks, C 1s peak of 282.5 eV, Ti 2p_{3/2} peak of 455.1 eV and Ti 2p_{1/2} peak of 461.2 eV. The oxygen and nitrogen peaks are inconclusive. Due to the very high chemical affinity of Ti for oxygen and

nitrogen, these gases may incorporate into the TiC films during film deposition as a result of interactions with residual gases in the vacuum.

5.5 Concluding remarks

TiC films prepared by this technique were stoichiometric as evident from XPS measurements. After etching about 170 Å deep into the surface the measurements showed strong signals for TiC with minimal oxygen signals. Isolated nitrogen signals are also present in the films. Presence of oxygen at the surface and nitrogen in the film was attributed to the very high chemical affinity of titanium for these gases. Nitrogen gas is mainly used in breaking vacuum inside the deposition chamber; it is therefore not unexpected that this gas is detected in the film.

It has been shown that the sputter rate depends on the RF power. An RF power of 200 W was used for the preparation of films for SBS measurements. At this power the sputter rate was measured as $12.2 \pm 0.1 \text{ nm min}^{-1}$. The densities and roughness of the films were measured using XRR. The measured density for films prepared at different RF powers was lower than the bulk density. This is expected since it is generally accepted that most deposition techniques create film densities which deviate from the bulk density (Gürtler *et al.*, 1989; Hüppauff *et al.*, 1993). The measured low roughness implies that the films were of high quality. Surface quality is very crucial in SBS measurements. Smooth surfaces produce less elastically scattered light which will enhance the detection of weak inelastic scattering peaks.

The crystallinity of a film is also an important aspect in the final performance of the coating. Crystallinity of hard coatings is directly correlated to the substrate temperature during deposition (Portolan *et al.*, 2009). The higher the substrate temperature, the higher the crystalline order of the coating. Mani *et al.*, 2005 reported that the sputtering pressure had an influence on the substrate morphology and chemical composition of the TiC films prepared using RF sputtering. It was observed that the film structure gradually changed from a mixture of distorted TiC at lowest pressure, 0.35 Pa, to homogeneous TiC at higher pressure, 1 Pa, with preferential orientation [111]. All the films prepared in this work were prepared at 6×10^{-3} mbars (0.6 Pa) with no substrate heating. GIXRD measurements showed that there was no preferential orientation for the films prepared at different powers. Only a random distribution of crystallites was observed. This is consistent with results reported by Mani *et al.*, 2005.

Pang (1997) found that the general elastic properties of polycrystalline aggregate with random distribution of anisotropic crystallite of any symmetry classes are the same as those of isotropic materials. We can therefore conclude that only two non-independent elastic constants (isotropic case) will be determined for the TiC films instead of five effective elastic constants (polycrystalline aggregates with preferred orientation) as shall be discussed in Chapter 6.

Chapter 6

Elastic Properties of Titanium Carbide Films

6.1 Introduction

The coating of cutting tools is of great importance for industrial machining as performance of these tools can be increased noticeably by coating the tool bits. Titanium carbide (TiC) coatings are widely used in such applications owing to their excellent properties, such as high thermal and chemical stability (except in oxidizing acids), high thermal conductivity, high hardness and strength and good corrosion resistance. Typical applications of TiC coatings include cutting and milling tools, use on ball bearings to improve their hardness and lower the coefficient of friction (Soldán and Musil, 2006) and for corrosion resistance on metallic structures. However, Ti-based alloys have poor oxidation resistance at high temperatures (Hou *et al.*, 2008). This limits the highest operating temperature for components made of Ti-based alloys to about 550 °C (Vojtěch *et al.*, 2003).

There has been extensive research on the structure, morphology and chemical composition of TiC films, as outlined below. It is known that TiC crystallises in the NaCl type structure similar to TiN (Mani *et al.*, 2005; Kataria *et al.*, 2010). The structure and mechanical properties of a TiC film can be influenced by deposition parameters such as substrate bias, RF power, deposition pressure and temperature (Obata *et al.*, 1982; Mani *et al.*, 2005; Soldan and Musil, 2006; Aguzzoli *et al.*, 2010) or by addition of gases such as oxygen (Marques *et al.*, 2007). The elastic properties of thin films therefore depend on the deposition conditions.

Elastic properties provide useful information concerning fundamental interactions within the material, thus enabling interatomic potentials to be developed for computational modelling of materials with superior qualities. Elastic stiffnesses are related to the engineering moduli used to describe bulk mechanical properties. A study of these properties therefore leads to information that is of practical value to both the physicist and the engineer. Several techniques have been used thus far to measure elastic properties of materials, in particular, elastic stiffnesses. These include, among others, the ultrasonic method (Pollard, 1977; Schreiber *et al.*, 1973), the resonance method (Anderson *et al.*, 1992), the photo acoustic method (Aussel and Monchalin, 1989), particle and x-ray scattering (Clausen *et al.*, 1985) and scanning acoustic microscopy (Mendik *et al.*, 1992). In the present Chapter the elastic properties of titanium carbide films deposited on different substrates Si and SiC, are investigated using the surface Brillouin scattering (SBS) technique. The measured SBS results are presented in Section 6.2. The results are then used to

extract the elastic stiffnesses of TiC films in Section 6.3. Discussion of the results follows in Section 6.4. The chapter ends with an analysis of the effects of varying deposition parameters on the elastic properties of the films (Section 6.5) and conclusions (Section 6.6)

6.2 Measured SBS spectra for TiC films

A particular combination of over-layer and substrate determines the types of excitations, localised near the surface, which can be observed by the surface Brillouin scattering technique. These SBS-observable excitations include among others, Rayleigh surface acoustic waves (RSAWs), Sezawa waves (SWs), pseudo Sezawa waves (pSWs) and Stoneley waves.

The two main categories of thin supported films, namely fast on slow and slow on fast, and their further classification into strongly and weakly stiffened or loaded systems have been discussed in Chapter 4. The results presented here are for *TiC/Si* and *TiC/SiC* which have been classified (in Chapter 4) as weak fast on slow and weak slow on fast systems, respectively, based on calculations in which the elastic properties of the TiC films are determined from Voigt-Reuss-Hill averaging procedures for polycrystalline films and employing the elastic stiffnesses of single crystal TiC as discussed in Chapter 4.

6.2.1 Fast on slow system (*TiC/Si*)

A series of SBS measurements have been carried out on the *TiC/Si* system for film thicknesses ranging from 50 nm to 600 nm. All the films were prepared at 200 W RF power. Figure 6.1 shows a representative measured surface Brillouin spectrum for a film of thickness 500 nm in which $q_{||}d = 11.5$.

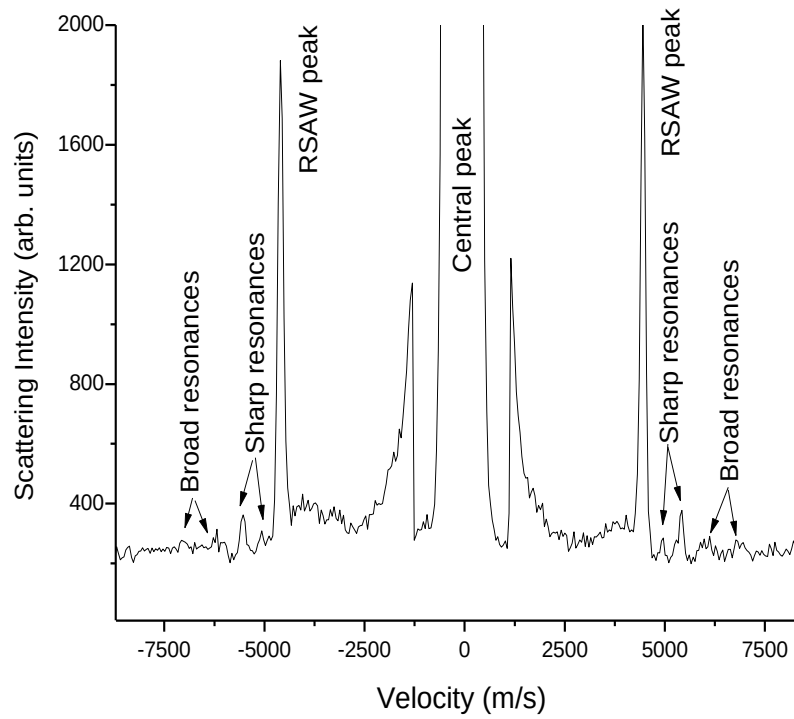


Figure 6.1: Measured SBS spectrum for a 500 nm ($q_{||}d = 11.5$) TiC layer on a Si substrate. Both anti-Stokes and Stokes bands are shown. An intense RSAW is visible together with both sharp and broad features. The “Central peak” is the elastic peak resulting from elastically scattered light and is unshifted in frequency.

Present in the spectrum is a relatively intense central peak and the associated Stokes and anti-Stokes bands. The RSAW of TiC is clearly identified together with two sharp and two broad features.

Table 6.1 shows the respective film thickness d of the deposited TiC films and the corresponding value of $q_{\parallel}d$ obtained from equation (2.24) with incident angle θ_i constant at 71°

Table 6.1: Corresponding $q_{\parallel}d$ values for film thicknesses d for *TiC/Si*.

Film thickness (nm)	50	100	200	300	400	500	600
$q_{\parallel}d$	1.2	2.3	4.6	6.9	9.2	11.5	13.9

Figure 6.2 shows typical measured results for the scattering intensity as a function of frequency shift, for the layer thickness given in Table 6.1 above. The spectra are identified by their respective $q_{\parallel}d$ values (as in Table 6.1). It is observed that, in addition to the RSAW which is dominant, other lower-intensity peaks appears at larger frequency shifts (> 16 GHz) for $q_{\parallel}d \geq 4.6$.

A stiffening system is characterised by the film having a stiffening effect on the SAW velocity, i.e., with increasing layer thickness this velocity increases from the RSAW velocity of the substrate and levels off at the RSAW velocity of the film. This is clearly visible in the measured dispersion curve for the *TiC/Si* system in figure 6.3. The dispersion was obtained by varying d whilst θ_i was kept constant at 71° .

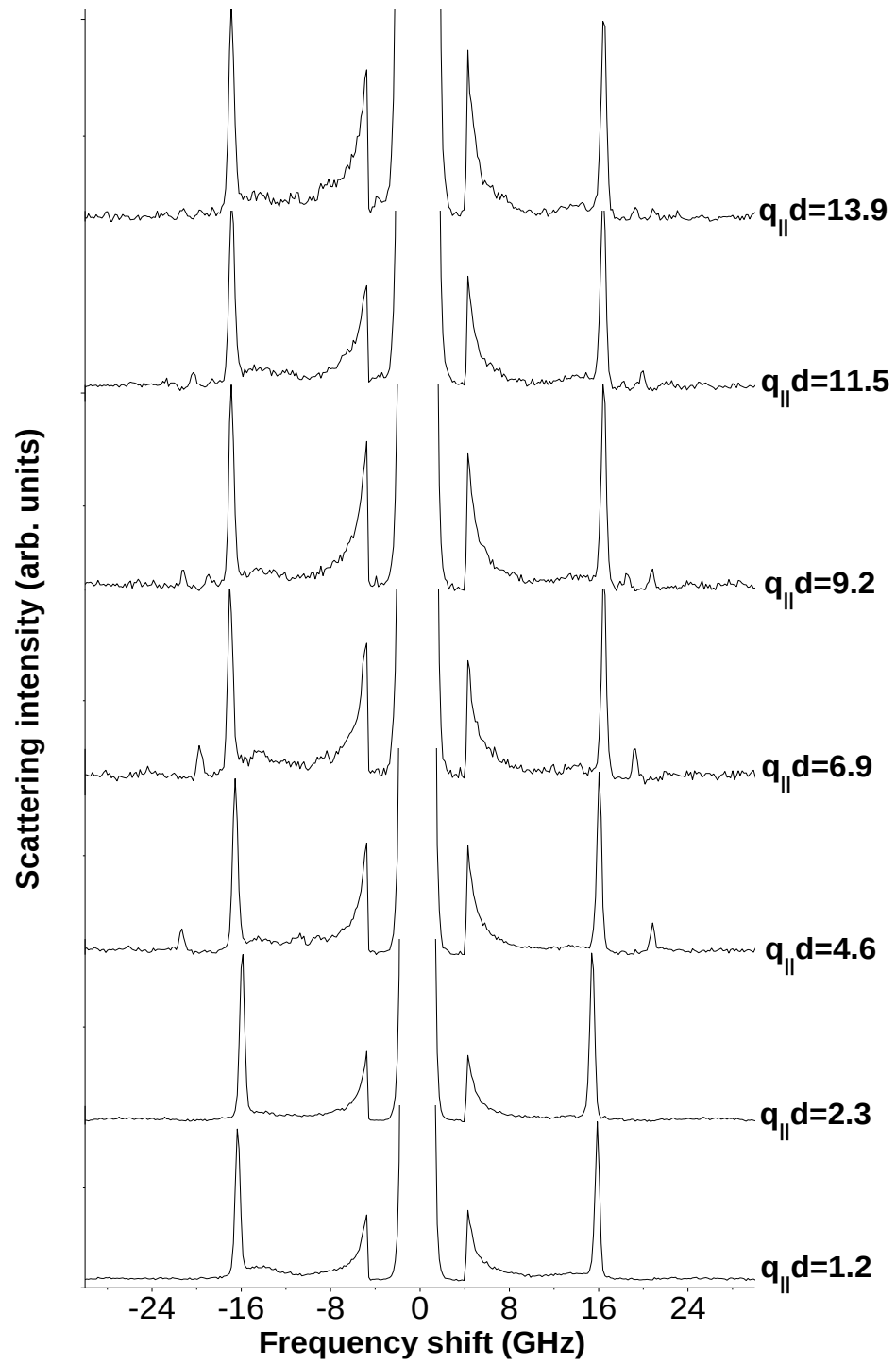


Figure 6.2: Typical measured SBS results for scattering intensity as a function of frequency shift for TiC films on silicon substrates.

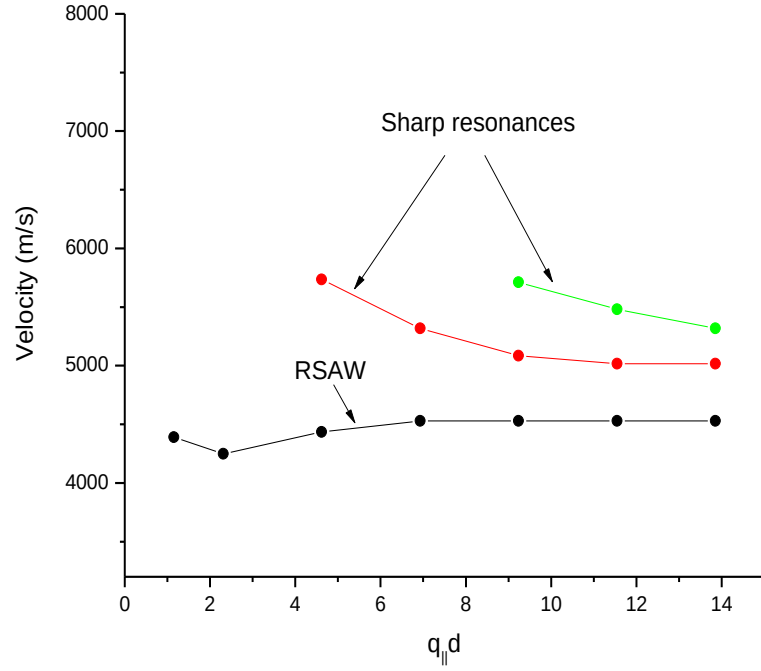


Figure 6.3: Measured velocity dispersion of the modes vs. $q_{||}d$ for the *TiC/Si* system. The dispersion was obtained by varying the layer thickness d while keeping $q_{||}$ constant i.e., θ_i was kept constant at 71° .

From figure 6.3, the measured Rayleigh velocity of TiC, 4530 m/s, is considerably lower than the calculated value of 5600 m/s. This implies that the measured elastic properties (stiffnesses) for TiC films are significantly lower than the ones used in calculations.

6.2.2 Slow on fast system (*TiC/SiC*)

A series of SBS measurements have been carried out on the *TiC/SiC* system for film thicknesses ranging from 50 nm to 600 nm. Figure 6.4 shows a representative surface Brillouin spectrum as measured for a 500 nm TiC layer on a SiC substrate.

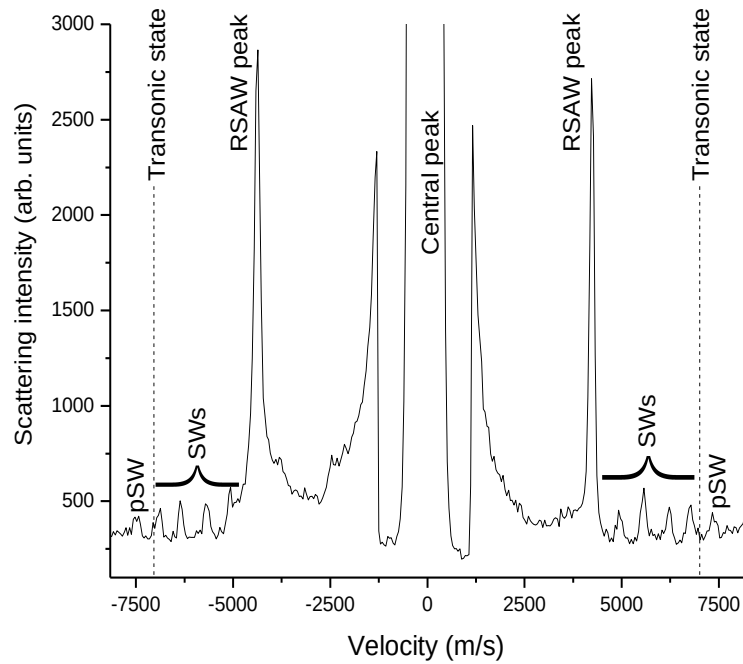


Figure 6.4: Measured SBS spectrum for a 500 nm ($q_{\parallel}d = 11.5$) TiC layer on a SiC substrate. Anti-Stokes and Stokes bands are shown. An intense RSAW is visible together with SWs and a pSW. The “Central peak” is the elastically scattered peak.

The relatively intense central peak and associated Stokes and anti-Stokes bands are present, together with inelastic scattering peaks from the RSAW, SWs and a pSW which lies in the region above the transonic state (Chapter 4).

The 6H-SiC (0001) substrate used in this work is transparent. In transparent solids, the elasto-optic scattering mechanism is dominant (Chapter 2) and therefore, if a transparent substrate is used elasto-optic scattering cannot be ignored (Bortolani *et al.*, 1983; Marvin *et al.*, 1980). The SBS results (Fig. 6.5) for $q_{\parallel}d = 1.2$ (layer thickness of 50 nm) clearly show a broad feature around 13 GHz. This feature is assumed to be associated with the elasto-optic contribution from the substrate. The elasto-optic scattering mechanism is beyond the scope of this thesis and therefore only SBS measurements for films with $q_{\parallel}d \geq 4.6$ (layer thickness of 200 nm and greater) were used in the extraction of elastic stiffnesses.

Figure 6.5 shows typical measured results for scattering intensity as a function of frequency shift, for layer thicknesses in the range 50 nm to 600nm. The spectra are identified by their respective $q_{\parallel}d$ values as in Table 6.2.

Table 6.2: Corresponding $q_{\parallel}d$ values for film thicknesses d for *TiC/SiC* .

Film thickness (nm)	50	200	300	400	500	600
$q_{\parallel}d$	1.2	4.6	6.9	9.2	11.5	13.9

The dominant peak for each value of $q_{\parallel}d$ (≥ 4.6) corresponds to the RSAW. As $q_{\parallel}d$ is increased, the RSAW velocity first decreases and then levels off at 4320 m/s.

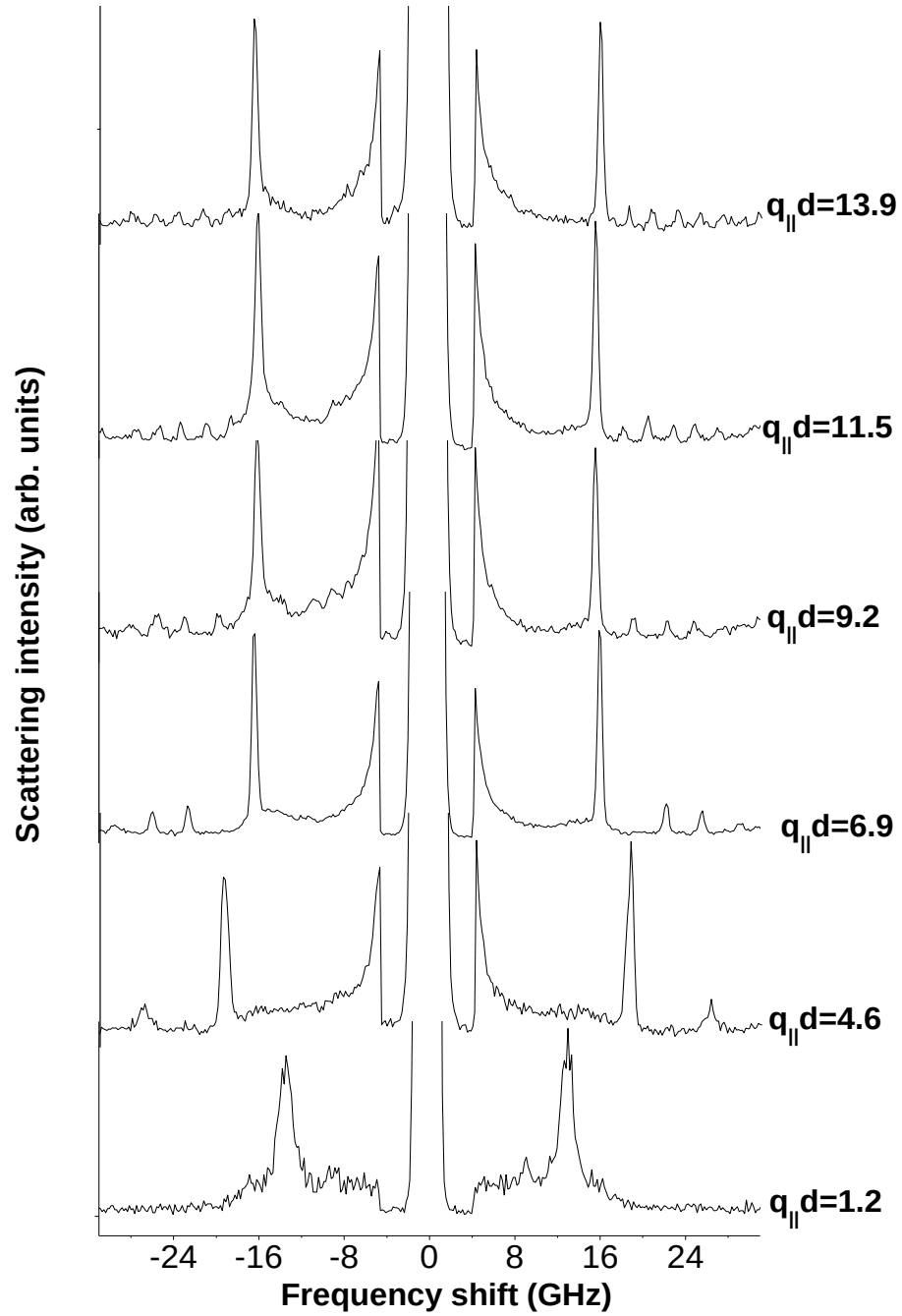


Figure 6.5: Typical measured SBS results for scattering intensity as a function of frequency shift for TiC films on a silicon carbide substrate. The broad feature at ~ 13 GHz is attributed to elasto-optic scattering.

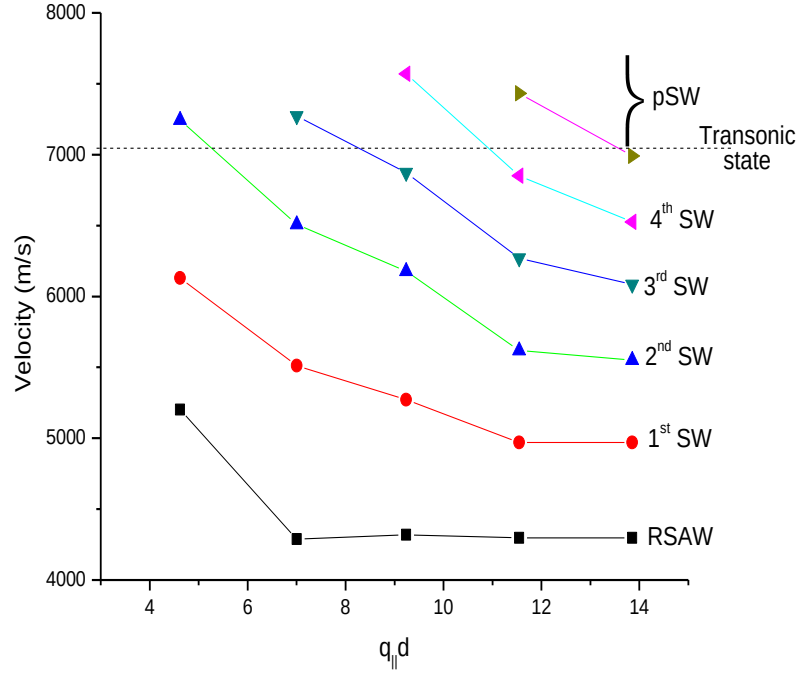


Figure 6.6: Measured velocity dispersion of the modes vs. $q_{||}d$ for the *TiC/SiC* system. The dispersion was obtained by varying layer thickness d . $q_{||}$ was kept constant by keeping θ_i at 71° .

In this loading system the presence of the layer leads to a reduction of the RSAW velocity and to formation of film guided modes known as SWs and pSWs. For $q_{||}d = 4.6$ only one SW is observed together with the Rayleigh, but as $q_{||}d$ increases more film guided modes are observed (up to five at $q_{||}d = 13.9$). The velocity dispersion of the modes as a function of $q_{||}d$ obtained from SBS measurements of five different layer thicknesses of TiC films is shown in figure 6.6.

6.3 Elastic stiffnesses of TiC films

From SBS measurements, elastic stiffnesses of the film are extracted by the simultaneous fitting of the dispersion curves (surface wave velocity, v , as a function of $q_{||}d$) for the observed modes. The process of fitting the dispersion curves is one of inversion. The best fit is obtained by a least-squares minimization procedure, namely

$$\chi^2 = \sum_{SAWs} (v_i^{meas} - v_i^{calc})^2 \quad (6.01)$$

This minimisation is with respect to variations of the elastic stiffnesses in which v_i^{meas} are the measured SAW velocities and v_i^{calc} are the corresponding velocities determined from the surface Green's functions. When χ^2 value is a minimum, the elastic stiffnesses used to calculate v_i^{calc} are taken as the elastic stiffnesses of the film.

The dispersion relations of the modes can be obtained either by varying d whilst $q_{||}$ is kept constant or vice versa. The dispersion curves discussed in Section 6.2 were obtained by varying d . A larger data set was obtained for both systems by including SBS measurements of a 600 nm layer as a function of θ_i (30° to 80°). The results obtained from both varying d whilst keeping $q_{||}$ constant and varying $q_{||}$ with d constant, are shown in figures 6.7a and b. It is noted that the results for $q_{||}d = 9.2$ in figure 6.7b and the Raleigh point for $q_{||}d = 4.5$ are inconsistent for undetermined reasons. These data were excluded in the fitting procedures discussed below.

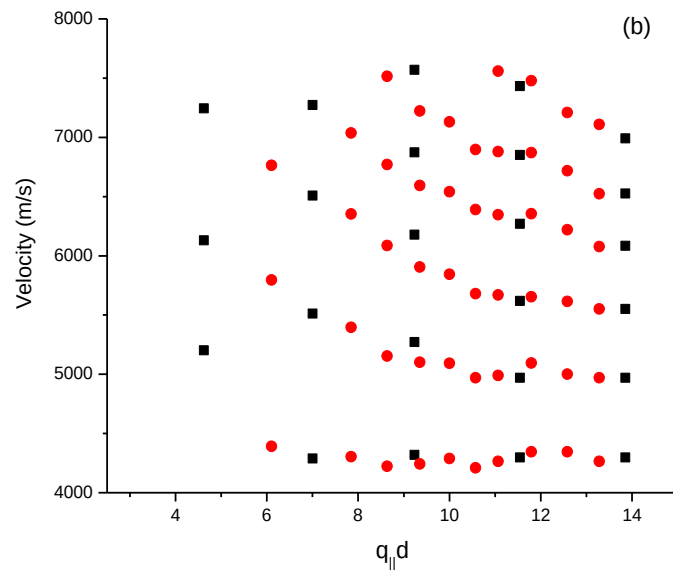
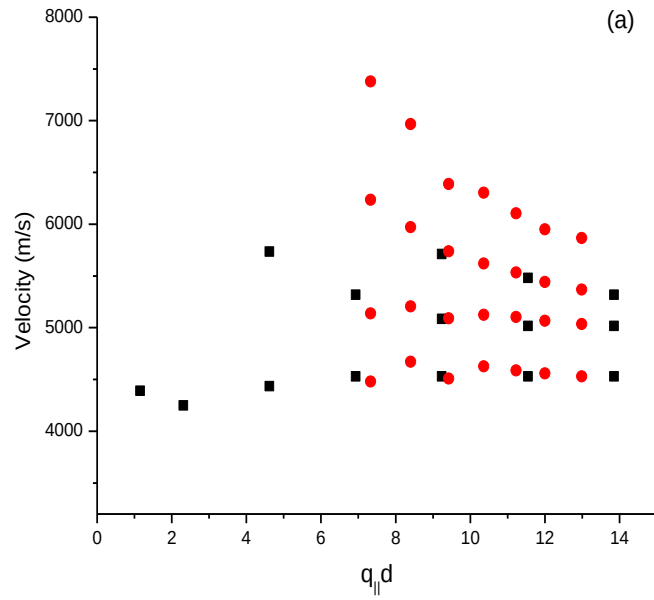


Figure 6.7: Velocity dispersion curves for (a) *TiC/Si* and (b) *TiC/SiC*. Black squares are results obtained from variation of d whilst red circles correspond to the variation of $q_{||}$.

Assuming an isotropic case, the Voigt-Reuss-Hill averaged elastic stiffnesses of TiC are $C_{11} = 492$ GPa, $C_{12} = 116$ GPa and $C_{44} = 188$ GPa. These have been calculated using single-crystal elastic stiffnesses of TiC: $C_{11} = 513$ GPa, $C_{12} = 106$ GPa and $C_{44} = 178$ GPa obtained from the literature (Pang, 1997). The averaged elastic stiffnesses were used as starting parameters in the minimization procedure on both systems. The resulting parameters are *TiC/Si*: $C_{11} = 270$ GPa, $C_{12} = 110$ GPa and $C_{44} = 83$ GPa and *TiC/SiC*: $C_{11} = 260$ GPa, $C_{12} = 104$ GPa and $C_{44} = 71$ GPa. Brillouin scattering intensities were then calculated using these elastic stiffnesses and compared to the measured SBS results. The results are presented in figures 6.8 and 6.9 for *TiC/Si* and *TiC/SiC*, respectively. As discussed above, the data for $q_{\parallel}d = 9.2$ and the Raleigh point for $q_{\parallel}d = 4.5$ shown in figure 6.7b for *TiC/SiC* are excluded in the fitting procedure. The density used in the fitting procedure for both systems is 3.4 g/cm^3 ; this was determined from X-ray reflectometry measurements (Chapter 5). Using the same elastic stiffnesses, SBS spectra were calculated (using Green's function methods) and these are compared to measured results in figure 6.10. In each case only the anti-Stokes portion of the SBS spectrum is shown, with the intense central peak omitted for clarity. The figures shows satisfactory agreement between measured and calculated velocities.

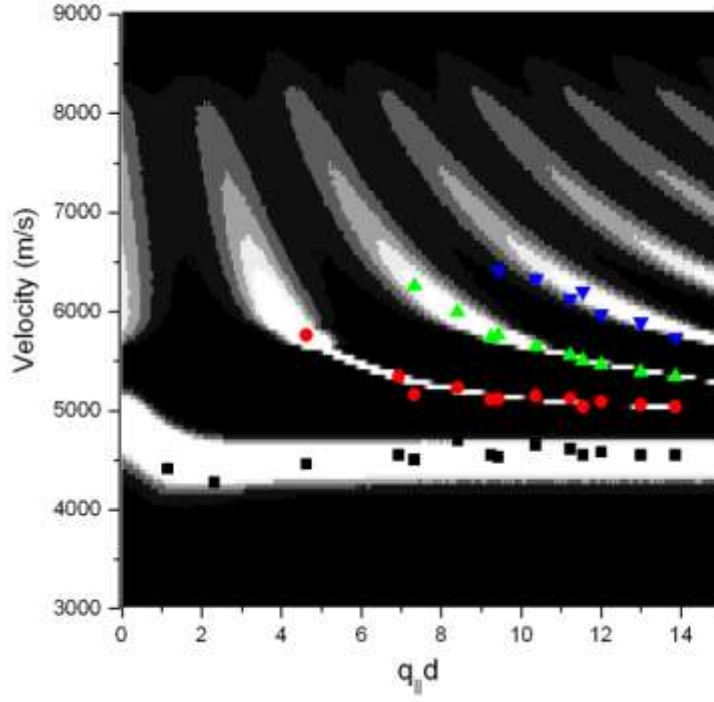


Figure 6.8: Brillouin intensities compared to the measured results for the *TiC/Si* system. The elastic stiffnesses resulting from the best fit are $C_{11} = 270$ GPa, $C_{12} = 110$ GPa and $C_{44} = 83$ GPa.

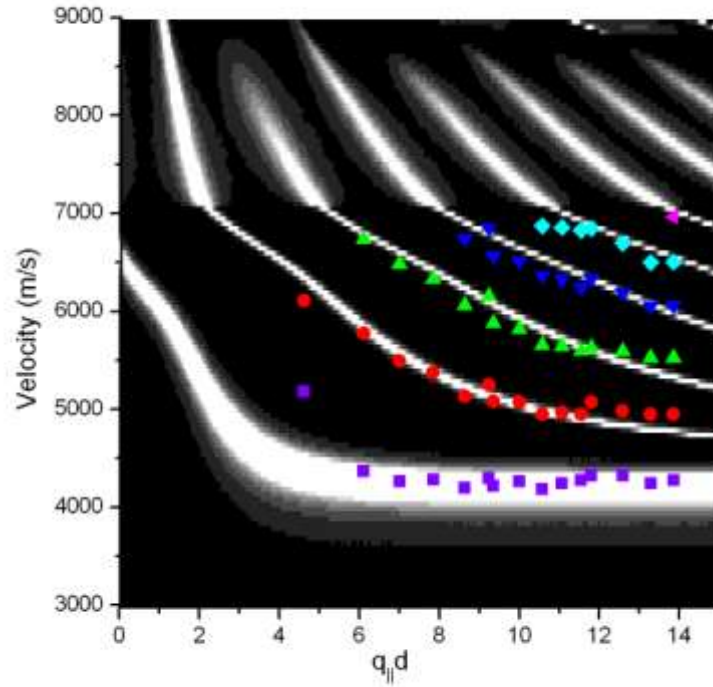


Figure 6.9: Brillouin intensities compared to the measured results for the *TiC/SiC* system. The elastic stiffnesses resulting from the best fit are $C_{11} = 260$ GPa, $C_{12} = 104$ GPa and $C_{44} = 71$ GPa

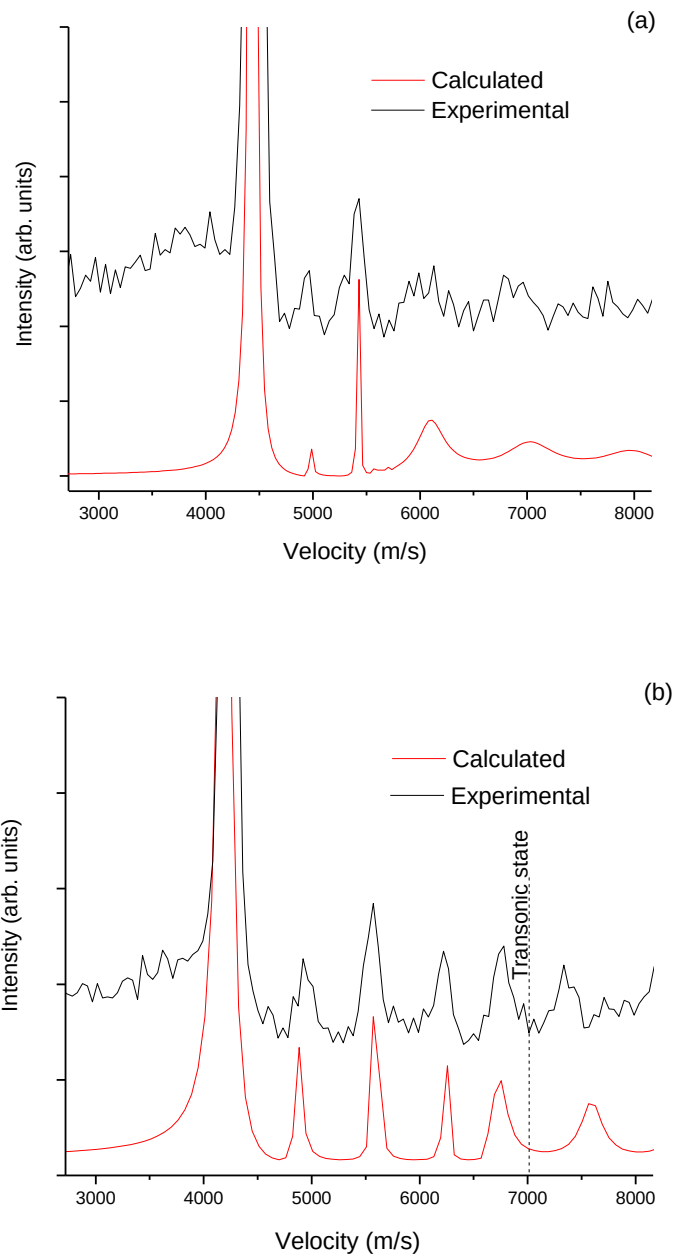


Figure 6.10: Calculated and measured SBS spectra for a 500 nm TiC film on a (a) silicon and (b) silicon carbide substrate. The calculated spectra use the values of elastic stiffnesses obtained from fitting of the dispersion curves.

6.4 Discussion

The elastic stiffnesses of TiC films determined from the two systems are presented in Table 6.3.

Table 6.3: Room temperature elastic stiffnesses of TiC films

	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)
<i>TiC/Si</i>	270 ± 3	83 ± 2	110 ± 3
<i>TiC/SiC</i>	260 ± 3	71 ± 2	104 ± 3
Deviation	4%	14%	5%

These elastic stiffnesses have been determined using the least squares fitting to the phase velocities of the observed modes. This procedure has been successful in many cases (Mutti *et al.*, 1995; Beghi *et al.*, 1997; Wittkowski, *et al.*, 2004). In most of these cases a slow on fast system was desirable due to a wide range of observable-acoustic excitations. In the present work we have established that it is possible to extract elastic stiffnesses from a fast on slow system by using the Rayleigh and the sharp resonances.

In Chapter 5, it was stated that “GIXRD measurements showed that there was no preferential orientation for the TiC/Si films prepared at different powers. Only a random distribution of crystallites was observed. Pang (1997) found that the general elastic properties of polycrystalline aggregate with random distribution of anisotropic crystallite of any symmetry classes are the same as those of isotropic materials.

Examination of the relation $C_{12} = C_{11} - 2C_{44}$ expected for an isotropic film yields a 5% difference for TiC/Si that is considered reasonable agreement in terms of the accuracy of the fitting procedure, the deposition procedures on separate Si substrates and the size of the data set. It is thus suggested that the results for TiC/SiC in which the relation breaks down with a disagreement of 13% could indicate a degree of anisotropy in the TiC films in this case. Further work using GIXRD is necessary to confirm this conclusion. As an alternative explanation, there may be differences in bonding between the TiC film and the respective substrates, namely Si and SiC that can lead to serious errors in any type of fitting procedure (Nizzoli *et al.*, 1998). Bonding differences were also discussed by Yu *et al.* (1990), where both perfect bonding and frictionless bonding were considered in relation to the indentation technique

In conclusion the discrepancy in the elastic stiffnesses determined from two systems, *TiC/Si* and *TiC/SiC* is not unexpected. The categories presented in Chapter 4 are defined by the relative (film to substrate) shear wave velocities. The shear wave velocities are obtained from calculations that rely on averaged elastic stiffnesses obtained from the single crystal elastic stiffnesses. From the results just presented for *TiC/SiC*, it appears that a more accurate category breakdown would be achieved if film parameters are used instead. The revised category (based on experimentally obtained velocities; figure 6.9) for *TiC/SiC* is strong slow on fast rather than weak slow on fast. *TiC/Si* is still categorised as weakly fast on slow system.

6.5 Effect of deposition conditions on the elastic properties of TiC films

Theoretical studies of film growth and experimental evidence show that there is a direct link between the energetics of the deposition process and the film microstructure, which in turn determine the nature and magnitude of intrinsic stress. Fundamental quantities in the deposition process are the particle flux density and the resulting energy striking the condensing film, both of which are functions of many parameters such as bias voltage, RF power, target to substrate distance, deposition temperature, pressure and substrate orientation (Windischmann, 1992). Deposition conditions determine film composition and lead to important consequences in the development of residual stress. The effects of two deposition parameters, bias voltage and RF power, are considered here.

6.5.1 Bias voltage

It has been argued that depending on the value of the bias voltage several phenomena, such as etching, densification and re-sputtering can occur during a non-reactive sputtering process (Zhang *et al.*, 2008). An increase in the negative bias voltage enhances the kinetic energy and the flux of the incident positive ions. Higher negative bias voltage can induce additional effects such as re-sputtering and lattice defects (Medjani *et al.*, 2005). These authors observed that, hardness of films

deposited at room temperature decreases with increasing negative bias voltage while that of films deposited at a higher temperature increases.

A 550 nm TiC film on a silicon substrate was prepared at a power of 200 W in an argon pressure of 6×10^{-3} mbars. The substrate was biased by a DC voltage of -70 V. Prior to deposition of this film, the growth rate at these deposition conditions was established as 9.9 nm/min. This is lower than the deposition rate for films prepared with no bias voltage, i.e., 12.2 nm/min. This may imply that re-sputtering is occurring at the substrate bias of -70 V.

SBS measurements on this film were carried out as functions of the angle of incidence, 30° to 70° ($q_{\parallel}d$ from 6.7 to 12.6). The results are shown in figure 6.11. The square points represent films grown at zero bias while the open circles represent results from a film grown under -70 V substrate bias. The results for zero bias are the ones presented in Section 6.2.1 but limiting the plotted points to those in which $q_{\parallel}$ was varied. There is a clear upward shift in the dispersion curves upon substrate biasing. This increase in phase velocity is attributed to stiffening in the film due either stress build-up or changes in microstructure. The elastic stiffnesses of this stressed film were determined using the fitting procedure described in Section 6.3.

In figure 6.12, the Brillouin intensities calculated using elastic stiffnesses obtained from the best fit are compared to experimental measurements. The best fit clearly reveals that the experimental data points indicated by red circles have to be assigned to the second mode. One of the reasons why the first mode might not be visible is a very small scattering cross section (Wittkowski *et al.*, 2000). As a result,

weak signals will be difficult to resolve in the Brillouin spectrum. The Green's function calculation shows that the first mode is very weak (Fig. 6.12).

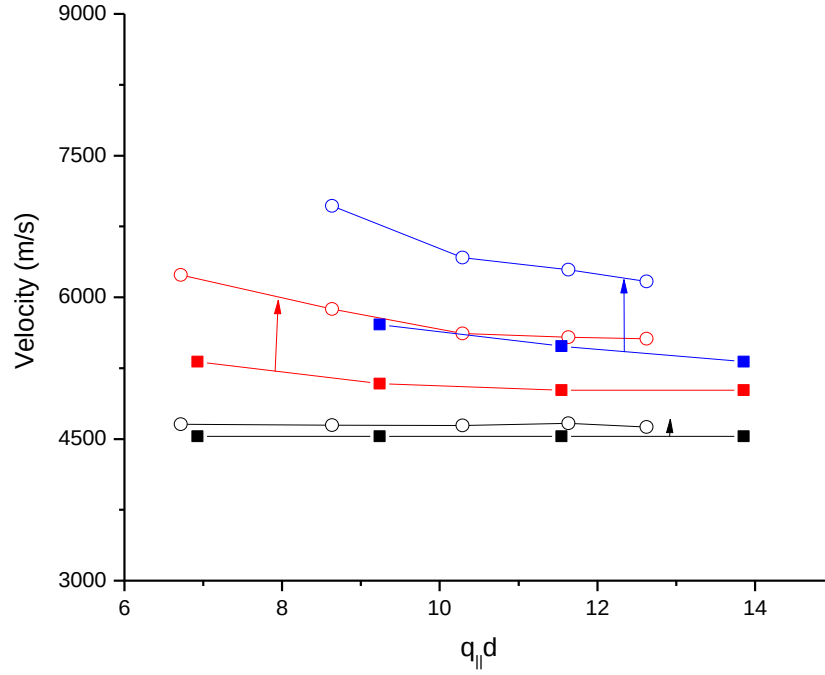


Figure 6.11: Velocity dispersion curves of TiC films deposited on silicon substrates under different substrate bias. Results from films with zero bias are represented by squares and those with -70 V bias by circles.

Table 6.4: Comparison of elastic stiffnesses of TiC films obtained from a 0 V and -70 V substrate bias.

	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)
0 V	270 ± 3	83 ± 2	110 ± 3
-70 V	277 ± 3	88 ± 2	115 ± 3

Table 6.3 shows that the elastic stiffnesses for the TiC film on a negatively biased substrate are consistently higher than those for an unbiased substrate. The shift in phase velocity and consequent shift in elastic stiffnesses is due to the stiffening of the film. The direct correlation between the elastic stiffnesses and stress is yet to be established since compositional changes may also have an influence. The separation of these two influences awaits a careful examination using the variety of techniques discussed in Chapter 5.

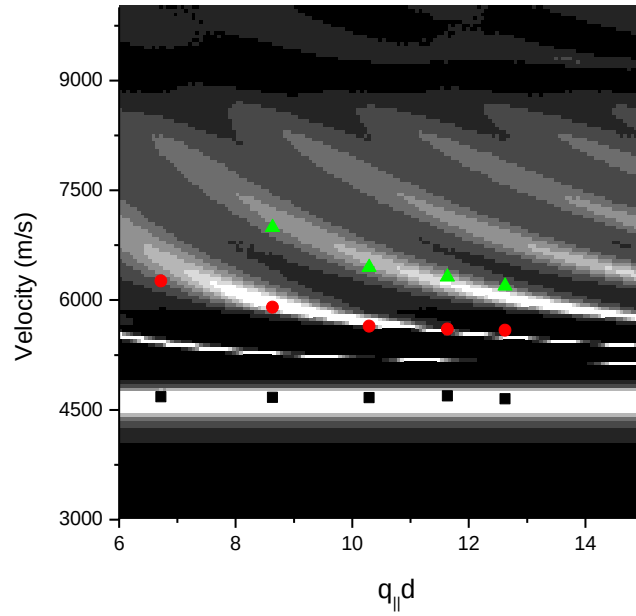


Figure 6.12: Brillouin intensities compared to the measured results for a 550 nm TiC film on a silicon substrate, prepared at a substrate bias of -70V. The elastic stiffnesses resulting from the best fit are $C_{11} = 277$ GPa, $C_{12} = 115$ GPa and $C_{44} = 88$ GPa.

6.5.2 RF power

A number of workers (Rahmane *et al.*, 2010; Kim *et al.*, 2010; Nair *et al.*, 2011) have found that RF power mainly affects the electronic and optical properties of films. On the other hand, some researchers (Yang *et al.*, 2009) have reported that phase formation and crystallinity in films may also be a direct result of the applied RF power. Studies of stress as a function of RF power were done by Rahmane *et al.*, (2010). They observed that the intrinsic compressive stress decreased with both increasing RF power and gas pressure, and near stress free films were obtained at a power of 200 W and an argon pressure of 2×10^{-3} mbars.

Essentially, RF power affects the growth rate. Variation of growth rate with RF power for TiC films was presented in Chapter 5. Using the growth rates in Table 5.2, five TiC films, each of layer thickness $d = 350$ nm were deposited on silicon substrates at different RF power settings (50 W, 100 W, 150 W, 200 W and 250 W). SBS measurements for the films are shown in figure 6.13.

Three peaks in addition to the Rayleigh peak are observed for 50 W compared to only two additional peaks for the other RF power settings. One possible reason for this is that the film prepared at 50 W could be elastically softer than the silicon substrate. In this context it is noted that there are three sharp peaks that may be due to true SWs as expected for a slow on fast system. Furthermore, as the RF power is increased the observed peaks shift to higher frequencies; this is a signature of stiffening in the film. Further work is necessary to investigate the true nature of the film/substrate system

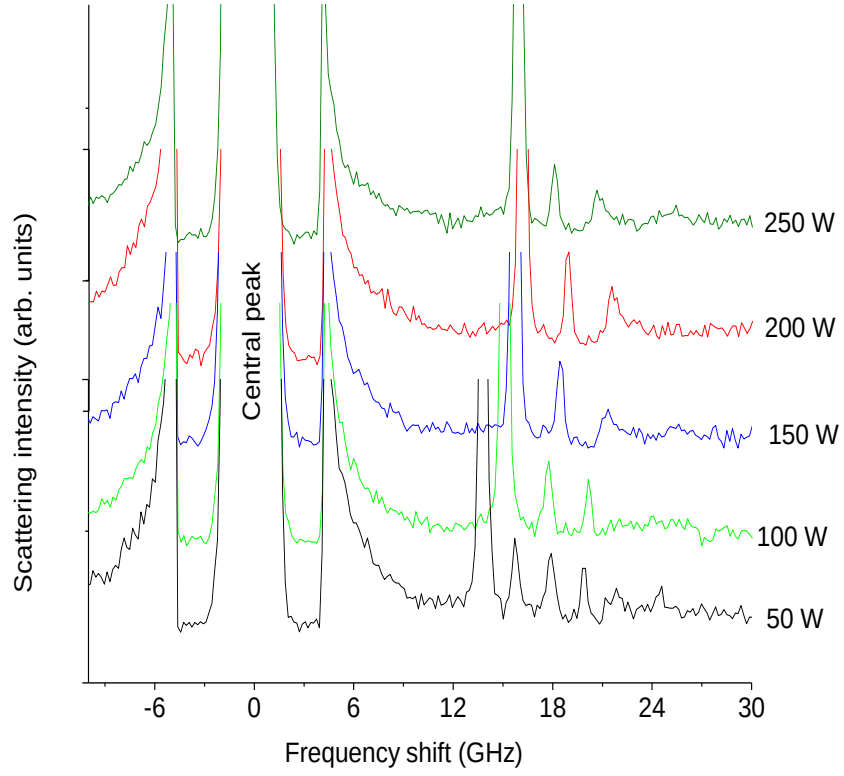


Figure 6.13: Measured SBS spectra for scattering intensity as a function of frequency shift for TiC films (of layer thickness 350 nm) on a silicon substrate prepared at different RF powers. Only the anti-Stokes peaks are shown here for clarity.

Chapter 7

Platinum Group Alloys: Rh_3Zr and Rh_3Nb

7.1 Introduction

Gas turbine engines have been widely used in industry for many years. They are useful in aircraft jet engines and in electricity generation. The high temperature conditions which they are subject to daily have necessitated the search for new materials with superior high-temperature capabilities and properties than the traditional nickel based superalloys. Nickel-based superalloys have long been used for the manufacture of gas turbines as they retain useful strength at temperatures of around 1000°C (Miura *et al.*, 2000; Zhang *et al.*, 2001). Nickel based superalloys have extremely high strengths at high temperatures because of the L_{12} -ordered particles (called γ') coherently embedded in a face-centred cubic (fcc) matrix (called γ) (Wenderoth *et al.*, 2006). The coherent interface prevents movement of dislocations.

In recent times, platinum based alloys have received increasing attention due to their exceptional high temperature properties and good oxidation resistances. High temperature Pt-based superalloys based on the fcc (γ) and $L1_2$ two-phase coherent phase structure (γ') have been developed by the National Institute for Materials Science (NIMS), Japan (Wenderoth *et al.*, 2006). Of the platinum group metals, Rh, Pd, Ir and Pt have the fcc structure, while Ru and Os have the hexagonal closed packed (hcp) structure. As a result, Rh, Pd, Ir, and Pt are promising candidates as base elements for new high and ultra high temperature alloys (Gornostyrev *et al.*, 2007). It has been found that the fcc/ $L1_2$ coherent two phase structure is formed in both Rh and Ir alloys which exhibit high strength of above 190 MPa at 1500 °C and 200 MPa at 1800 °C, respectively, as well as better oxidation resistance than the refractory alloys (Yamabe, 1997). However Rh-based alloys as compared to Ir-based alloys exhibit better oxidation resistance, lower thermal expansion coefficient, higher thermal conductivity and lower density (Chen *et al.*, 2004; Terada *et al.*, 2006); this makes them more promising for ultra high temperature gas turbine applications. Low thermal expansion coefficients and high thermal conductivity are desired for turbine blades to achieve excellent fatigue properties. Although the melting temperature of Rh, 1960 °C, is lower than that of Ir, 2447 °C, the lower density of Rh, 12.40 g/cm³, compared to that of Ir, 22.65 g/cm³, is advantageous (Yamabe, 1997).

The fcc structure of Rh can be equilibrated with the $L1_2$ structure in Rh-Am, Rh-Ce, Rh-Hf, Rh-Nb, Rh-Np, Rh-Ta, Rh-Th, Rh-Ti, Rh-Zr, Rh-V and Rh-U systems

(Massalski, 1986). Mechanical properties of Rh-based $L1_2$ intermetallic compounds were investigated by Miura *et al.* (2000). Micro-Vickers hardnesses of Rh_3Nb and Rh_3Ta were observed to be higher than that of the nickel-based alloy Ni_3Al at room temperature. This was attributed to the high work hardening rate of Rh_3Nb and Rh_3Ta . Both Rh_3Nb and Rh_3Ta showed a weak positive temperature dependence of strength unlike Ni_3Al which exhibits a strong positive temperature dependence of strength (a stress anomaly).

The present work investigates the elastic properties of the Rh-based alloys in the form of single crystals of Rh_3Zr and Rh_3Nb using the surface Brillouin scattering technique. To the best of our knowledge no experimentally measured elastic stiffnesses for Rh_3Zr and Rh_3Nb are available in the literature. However theoretical calculations using *ab initio* density functional theory (DFT) were reported by Chen *et al.* (2004).

The determination of the elastic stiffnesses of the Rh-based alloys will provide a scientific background for the development of superalloys based on the platinum group metals. Elastic stiffnesses provide information concerning the fundamental interactions occurring in solids. At high temperatures they can provide the interatomic potentials, which are principal parameters for thermodynamic calculations. Thermodynamic calculations and the associated phase diagrams based on them, provide a very effective way of developing superalloys based on platinum group metals.

7.2 Sample preparation

The Rh-based alloys Rh_3Zr and Rh_3Nb were supplied by the National Institute for Materials Science (NIMS), Japan. The Rh_3Zr sample was supplied in the form of an unoriented boule. A sample was cut from the larger specimen using the Metals Research Ltd. Servomet spark erosion facility available at the University of Johannesburg. The specimen was oriented until the [100] direction was within half a degree of the surface normal. This was done by sequentially lapping the sample on the grinding disc and taking Laue X-ray photographs. In order to obtain satisfactory surface Brillouin spectra, it was necessary to develop appropriate polishing techniques to attain the high reflectivity needed to sufficiently enhance the scattering cross-section. A high-quality surface was prepared for SBS measurements by mechanically polishing the surface down to $0.04\text{ }\mu\text{m}$ on an alumina impregnated disc. The polishing was done using the ENGIS Ltd. KENT 3 Automatic Lapping and Polishing Unit.

The second sample, Rh_3Nb , was supplied in the form of an oriented cube of $3\times 3\times 3\text{ mm}^3$. The orientation of the sample was confirmed by the Laue back-reflection X-ray technique and the (100) face was selected for polishing. Following successive polishing of the face with diamond grits starting from $6\text{ }\mu\text{m}$ down to $0.1\text{ }\mu\text{m}$, there was a substantial improvement in the quality of the Brillouin spectra. The final polishing stage was with $0.04\text{ }\mu\text{m}$ alumina grit and very satisfactory SBS spectra were obtained.

7.3 Density measurement using XRD

In calculating both the theoretical SBS spectra and the elastic stiffnesses, the density of the specimen must be known (section 2.3.3). The densities of both specimens were determined using X-ray diffraction as discussed in this section.

The plane spacing d and lattice parameter a of cubic single crystals of Rh_3Zr and Rh_3Nb were measured experimentally using the Philips PW. 1050 X-ray diffractometer, and the values were used to evaluate the density of Rh_3Zr and Rh_3Nb . The macroscopic density was also determined and compared with that from X-ray diffraction (XRD) measurements.

7.3.1 Theoretical aspects

Interference patterns formed in XRD originate from X-rays that are scattered by the electrons of atoms on various lattice planes within a crystalline solid. The relative phases of scattered X-rays depend critically on the separation between the planes. Constructive interference occurs when waves reflected on all successive planes satisfy the Bragg condition

$$n\lambda = 2d \sin \theta, \quad (7.01)$$

where n is the order of reflection, λ is the wavelength and θ is the Bragg angle. The lattice planes are indexed using Miller indices (hkl). The interplanar spacing d , for a cubic crystal, may be found from the following equation

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}. \quad (7.02)$$

Combining equation (7.02) and (7.01) and considering first-order reflection from the planes, we have

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2). \quad (7.03)$$

Equation (7.03) predicts all the possible Bragg angles at which diffraction occurs from the planes, for a particular incident wavelength λ and unit cell size a of a cubic crystal. Thus XRD allows us to determine the lattice parameter of a crystal's unit cell, and therefore its volume, together with the number of atoms in the unit cell.

Density ρ is given by

$$\rho = \frac{\sum A / N}{V}, \quad (7.04)$$

where A is the atomic number, N is Avogadro number and $V = a^3$ is the volume of a single unit cell.

7.3.2 Results and discussion

For the XRD measurements, a Cu-K α X-ray beam source of wavelength 1.542 Å isolated with a Ni foil filter, was used at 40 kV and 20 mA. Figure 7.1 shows the first order diffraction line at 46.23° for Rh₃Zr and 47.53° for Rh₃Nb. From equation (7.01) the plane spacing d is deduced as 1.96 Å and 1.91 Å for Rh₃Zr and Rh₃Nb, respectively. Laue X-ray method confirmed the {100} plane orientation for both crystals. The first order diffraction line can therefore be indexed to (200) for both crystals.

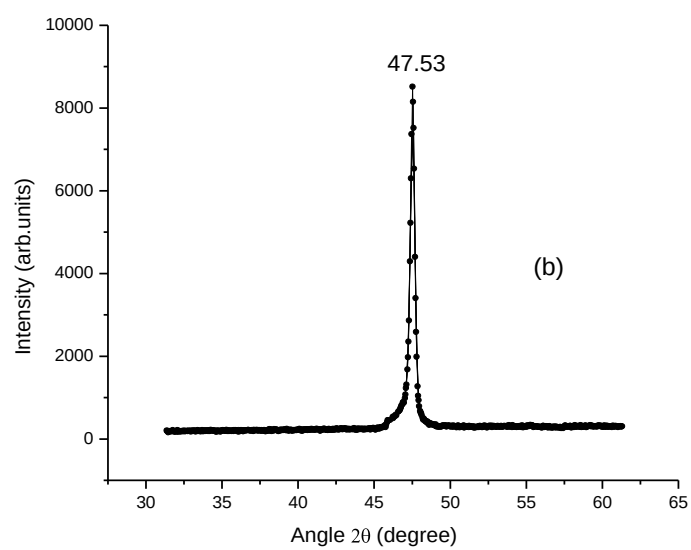
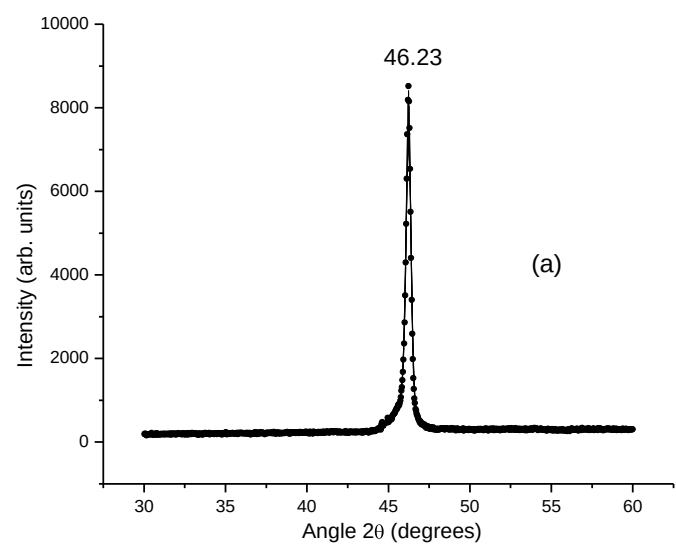


Figure 7.1: XRD measurements for (a) Rh_3Zr and (b) Rh_3Nb .

From equation (7.02) the lattice parameters for Rh_3Zr and Rh_3Nb are 3.92 Å and 3.82 Å, respectively. These values are comparable to those obtained by Chen *et al.* (2004) who reported experimental lattice constants of 3.927 Å and 3.857 Å for Rh_3Zr and Rh_3Nb , respectively. The number of atoms per unit cell of each specimen is four. The X-ray densities of Rh_3Zr and Rh_3Nb calculated using equation (7.04) are 10.97 g/cm³ and 11.87 g/cm³, respectively. For comparison purposes, the macroscopic density of each specimen was determined from the mass and the volume of each specimen using the Archimedes principle. The macroscopic density was obtained as 10.54g/cm³ for Rh_3Zr and 11.37g/cm³ for Rh_3Nb . The density determined from Archimedes principle is usually less than, and cannot exceed, the X-ray density, because the macroscopic specimen will usually contain minute cracks and pores. This is therefore in satisfactory agreement with the densities calculated here. X-ray densities were used for SBS calculations.

7.4 Room Temperature Elastic Stiffnesses of Rh_3Zr and Rh_3Nb

Two approaches have been developed to determine elastic stiffnesses using SBS. One approach involves the χ^2 minimization of the observed modes (Zhang *et al.*, 2001); the Rayleigh surface acoustic waves (RSAW), pseudo-surface acoustic waves (p-SAW) and longitudinal wave threshold (LW). The other is an analytical approach which involves the χ^2 minimization of secular equations for the Rayleigh surface acoustic wave and the longitudinal wave threshold velocities in the [100] and [110]

directions on the (001) surface of a cubic crystal. (Every *et al.*, 2010; Kotane *et al.*, 2011).

7.4.1 χ^2 minimization of the observed modes

The platinum alloys Rh₃Zr and Rh₃Nb have a large elastic anisotropy ratio and therefore their RSAW velocities have strong dependence on the wavevector direction. Accurate alignment of the laser beam in a chosen symmetry direction such as [100] is necessary for the evaluation of the angular dependence of the respective SAW velocities. For both samples, a series of SBS measurements were performed over a wide range of the azimuthal angle α , 0° to 360°, so as to obtain an angular variation of the SAW velocities (Fig. 7.2 and Fig. 7.6). From these measurements the [100] direction was established to within an angular variation of 2° for both specimens.

The relevant velocity thresholds in the SBS spectra for high symmetry directions enable one to calculate some of the elastic stiffnesses. For instance, in a [100] direction of a (001) plane of a cubic crystal, the longitudinal velocity threshold V_L is given by C_{11}/ρ (Chapter 1). A full set of elastic stiffnesses may then be extracted by the simultaneous fitting to the experimental results for the observed modes of surface wave velocity. The values of elastic stiffnesses obtained by DFT calculations (Chen *et al.*, 2004) were used as starting parameters in the fitting procedure.

The minimization of $\chi^2 = \sum_{SAW} (V_i^{meas} - V_i^{calc})^2 + \sum_L (V_i^{meas} - V_i^{calc})^2$ with respect to variations of the elastic stiffnesses was carried out. SAW (RSAW and p-SAW) velocities and the LW threshold (L) velocities about the [100] direction on the (001) plane of the single crystals were chosen for the minimization procedure.

(a) Rh₃Zr

SBS spectra were measured on the (001) surface of the Rh₃Zr alloy for the azimuthal angle α , ranging from 0° to 360° in steps of 5° to determine the [100] direction. The [100] direction is determined by fitting a sine curve and taking values of α corresponding to the minimum velocity. The results are shown in figure 7.2. The [100] direction corresponds to α values of 7°, 187° and 367°. α was reset to zero at $\alpha = 187^\circ$. Once this direction was determined, SBS measurements in the range of α angles between the [100] and [110] directions revealed the full velocity profile of the surface (Fig. 7.3). The velocities of both the RSAW and the p-SAW are strongly direction dependent on the (001) plane as is shown by their angular dispersion. The RSAW is dominant in the range of surface wavevector directions α in the interval 0° to 25° (e.g. figure 7.4(a) for $\alpha = 0^\circ$), beyond $\alpha = 5^\circ$ the RSAW is visible together with a low intensity p-SAW, (e.g. figure 7.4(c) for $\alpha = 10^\circ$). The Rayleigh peak reduces quite rapidly in intensity and velocity after $\alpha \approx 30^\circ$ as it finally degenerates into a slow transverse bulk wave at 45° yielding no normal displacements. The PSAW has a considerable surface character but loses energy to the bulk owing to its composition in which two of its partial waves are evanescent while the third is bulk-

like in nature (Zhang *et al.*, 2001). The p-SAW dominates in the range of α values from 30° to 45° .

The elastic stiffnesses of Rh_3Zr are determined using a least-squares fit of the experimental data to calculated results from the Green's function simulations of the surface dynamics. The RSAW and p-SAW data, while being sensitive to the elastic stiffness C_{44} and the combination $C_{11} - C_{12}$, is inadequate to provide the full set of independent elastic stiffnesses (Zhang, 2001). Additional information, which is usually obtained from the longitudinal bulk wave threshold within the Lamb shoulder, is needed to decouple the combination $C_{11} - C_{12}$.

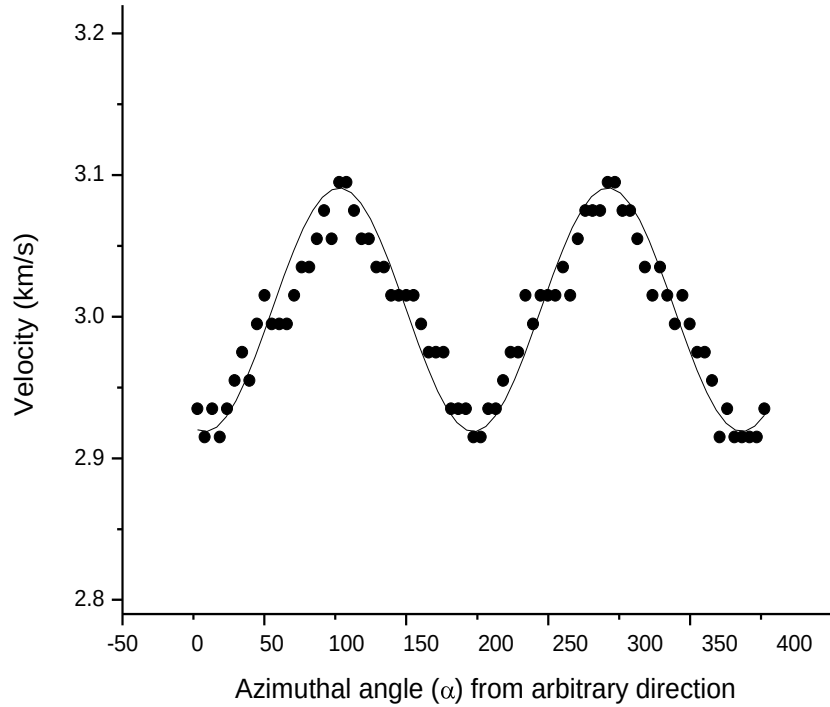


Figure 7.2: Angular dependence of the SAW velocities on the (001) surface of Rh_3Zr . A sine curve is fitted to determine the [100] direction. [100] direction occurs when $\alpha = 7^\circ$, 187° or 367° . α is reset to zero at $\alpha = 187^\circ$.

The additional measurement of the longitudinal dip provides the necessary sensitivity to the value of C_{11} such that, all three elastic stiffnesses are successfully recovered from the least squares fit. Figure 7.3 shows the best fit of measured to calculated velocities.

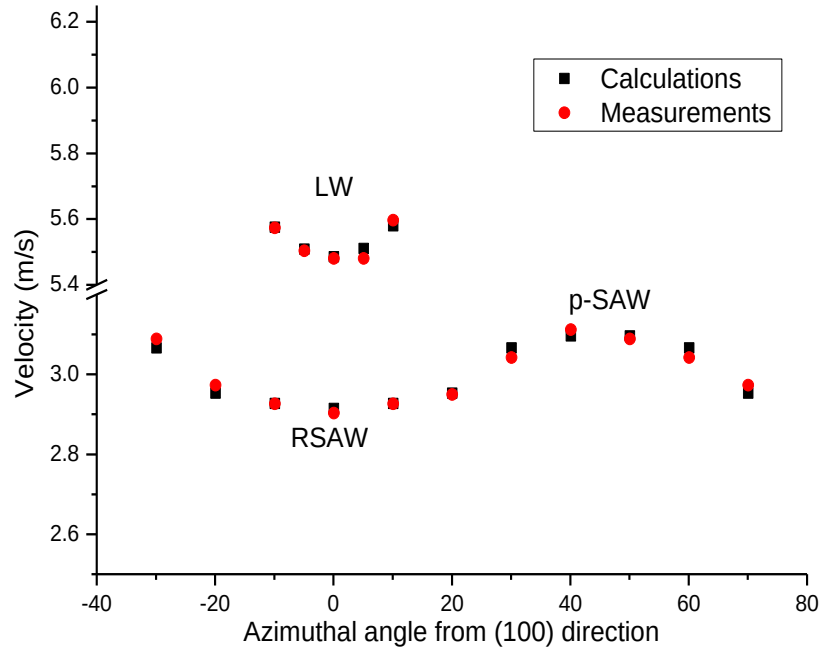


Figure 7.3: The directional dependence of the RSAW, p-SAW and LW velocities on (100) surface of Rh_3Zr . $\alpha = 0$ corresponds to 187° on figure 7.2. The elastic stiffnesses resulting from the best fit are $C_{11} = 329$ GPa, $C_{12} = 187$ GPa and $C_{44} = 145$ GPa.

A three dimensional plot of the variation of the χ^2 values with elastic stiffnesses, C_{11} and C_{44} using the fixed value of $C_{12} = 187$ GPa for Rh_3Zr is shown in figure 7.4. It is clear from the convergence of the C_{ij} values to yield a minimum value of χ^2 that the procedure results in an unambiguous set of elastic stiffnesses.

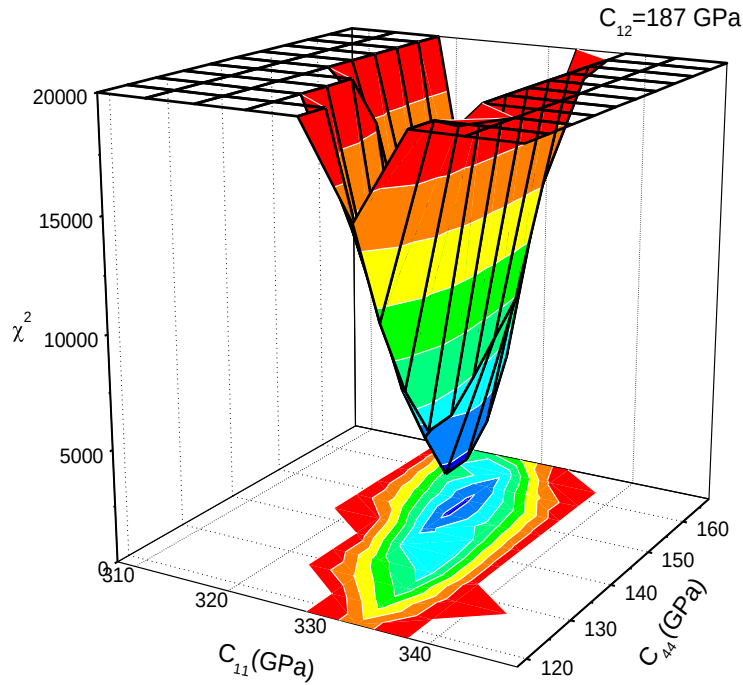
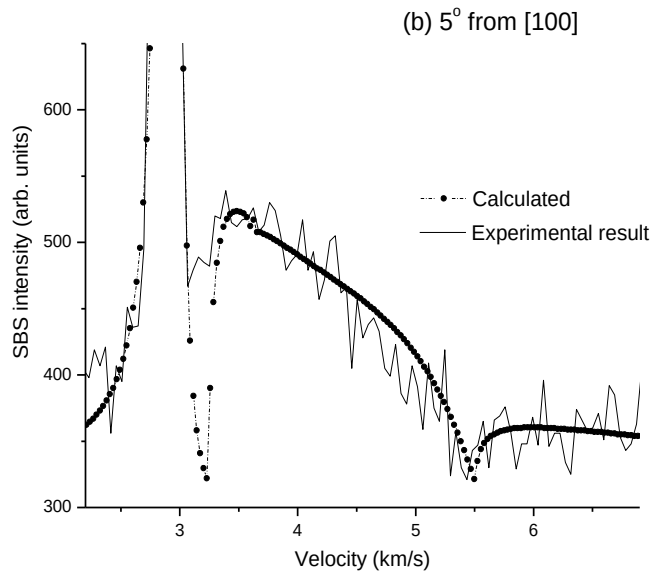
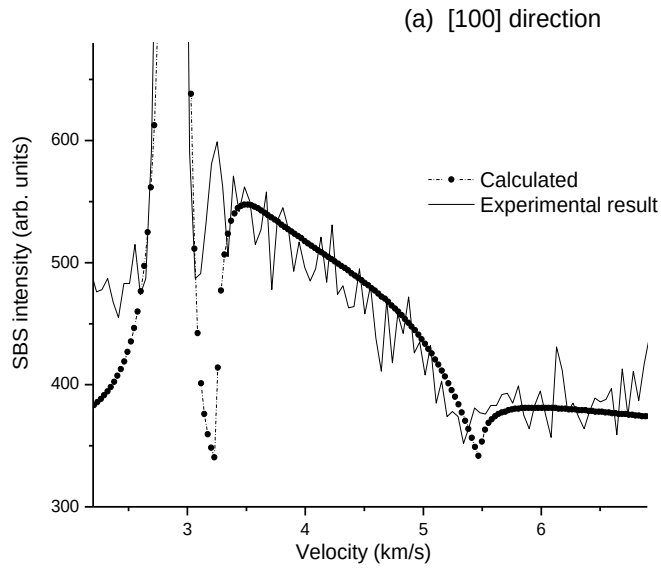


Figure 7.4: Three dimensional plot of the variation of the χ^2 values with elastic stiffnesses, C_{11} and C_{44} for Rh_3Zr . The values of the respective elastic stiffnesses converge to a minimum value of χ^2 .

The best fit and the contour plot (figures 7.3 and 7.4) yielded satisfactory room temperature elastic stiffnesses for Rh_3Zr , namely; $C_{11} = 329$ GPa, $C_{12} = 187$ GPa and

$C_{44} = 145$ GPa. Using these elastic stiffnesses, SBS spectra were calculated (using Green's function methods) and compared to the measured spectra as shown in figure 7.5. Figure 7.5 [(a), (b), (c) and (d)] show that there is good agreement between the measured and calculated SBS spectra in each of the wavevector directions.



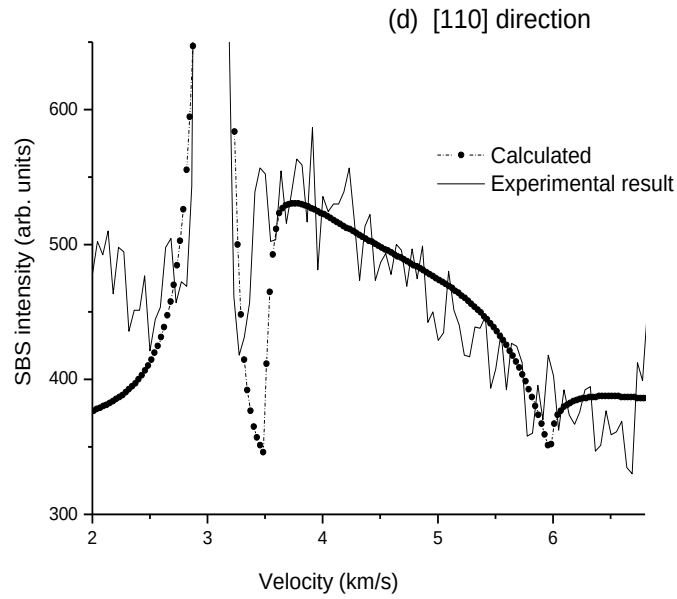
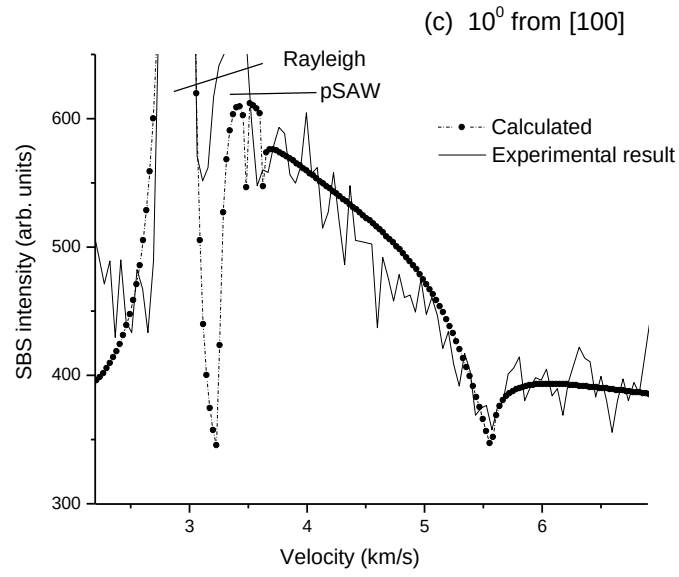


Figure 7.5: SBS spectra compared to calculated spectra for different directions (as indicated on each spectrum) from the [100] surface wave direction on the (001) plane surface of Rh_3Zr .

(b) Rh_3Nb

The directional dependence (Fig. 7.7) of the RSAW, p-SAW and LW velocities on (001) surface of Rh_3Nb has been obtained using the same procedure as for Rh_3Zr .

SBS measurements of the SAW velocities on the (001) surface of the Rh_3Nb alloy for the azimuthal angle α , ranging from 0° to 360° in steps of 10° (Fig. 7.6) were found to be adequate to fit the resulting sine curve in order to determine the [100] direction.

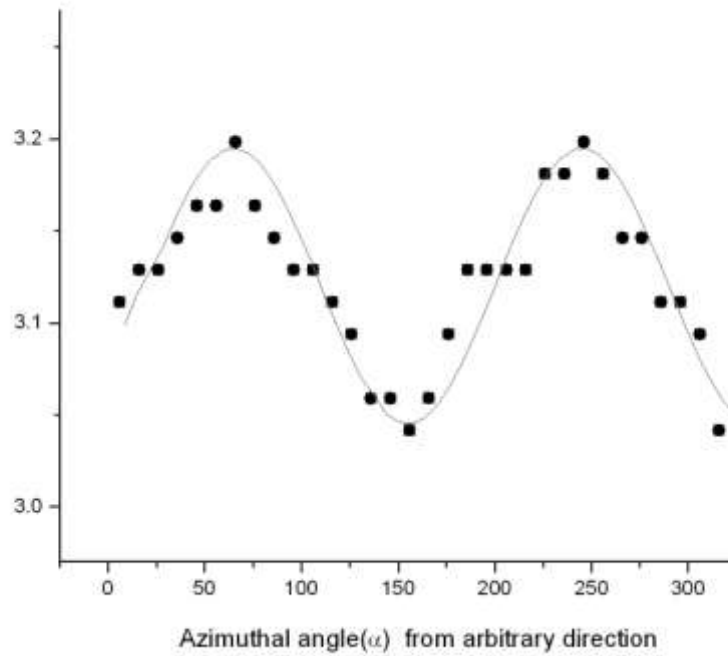


Figure 7.6: Angular dependence of the SAW velocities on the (001) surface of Rh_3Nb . SBS measurements were taken in steps of 10° . A sine curve is fitted to determine the [100] direction. [100] direction occurs when $\alpha = 156^\circ$ or 336° . α is reset to zero at this value 156° .

The elastic stiffnesses of Rh_3Nb was determined using a least-squares fit of the experimental data to calculated results from the Green's function simulations of the surface dynamics as discussed in part (a) for Rh_3Zr . To obtain all three elastic stiffnesses the longitudinal wave thresholds were used.

SBS measurements of the RSAW and p-SAW velocities taken in steps of 5° about the $[100]$ direction were used in the least squares fitting procedure (Fig 7.7). The SAW profile follows the same trend as for Rh_3Zr . The elastic stiffnesses resulting from the best fit are $C_{11} = 370$ GPa, $C_{12} = 186$ GPa and $C_{44} = 161$ GPa.

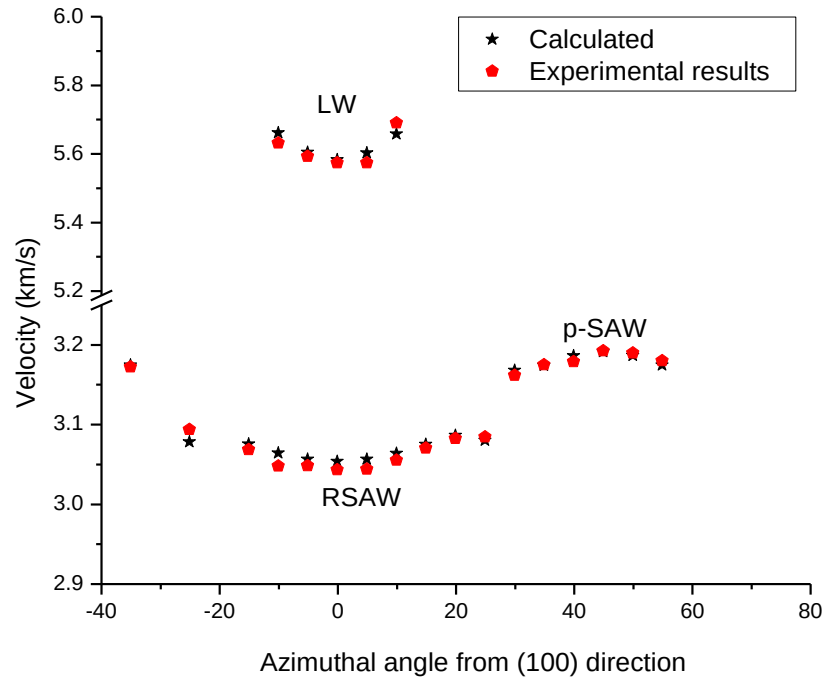


Figure 7.7: The directional dependence of the RSAW, p-SAW and LW velocities on (100) surface of Rh_3Nb . $\alpha = 0$ corresponds to 156° on figure 7.6. The elastic stiffnesses resulting from the best fit are $C_{11} = 370$ GPa, $C_{12} = 186$ GPa and $C_{44} = 161$ GPa.

A three dimensional plot for the variation of the χ^2 values with elastic stiffnesses, C_{11} and C_{44} for Rh_3Nb shows the convergence of the elastic stiffnesses to a minimum value of χ^2 (Fig. 7.8), giving an unambiguous set of elastic stiffnesses. The best fit and the contour plot (figures 7.7 and 7.8) yielded room temperature elastic stiffnesses for Rh_3Nb , namely; $C_{11} = 370$ GPa, $C_{12} = 186$ GPa and $C_{44} = 161$ GPa.

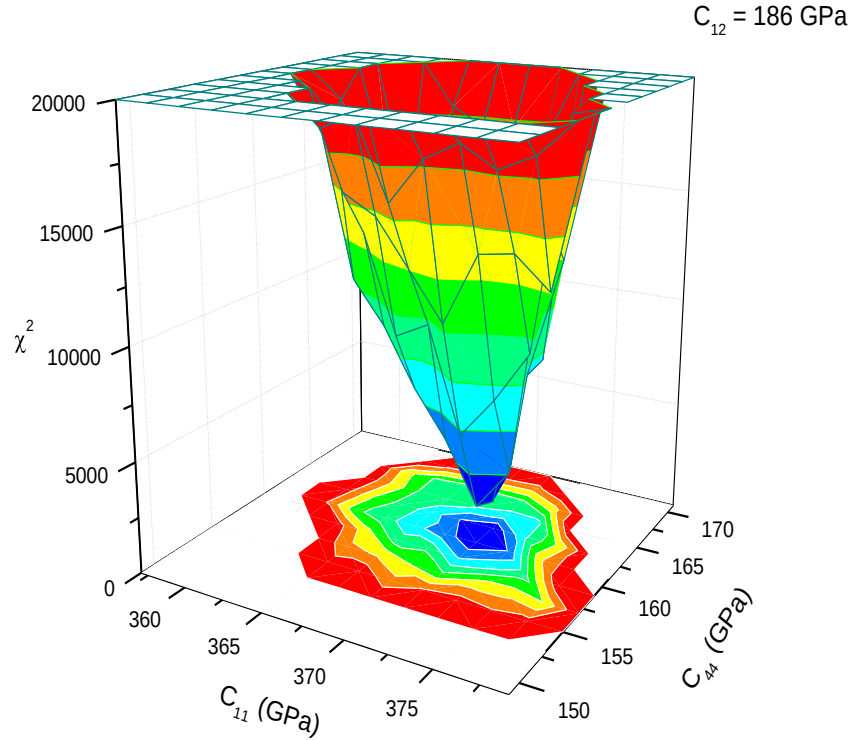


Figure 7.8: Three dimension plot of the variation of the χ^2 values with elastic stiffnesses, C_{11} and C_{44} for Rh_3Nb . The elastic stiffnesses converge to a minimum value of χ^2 .

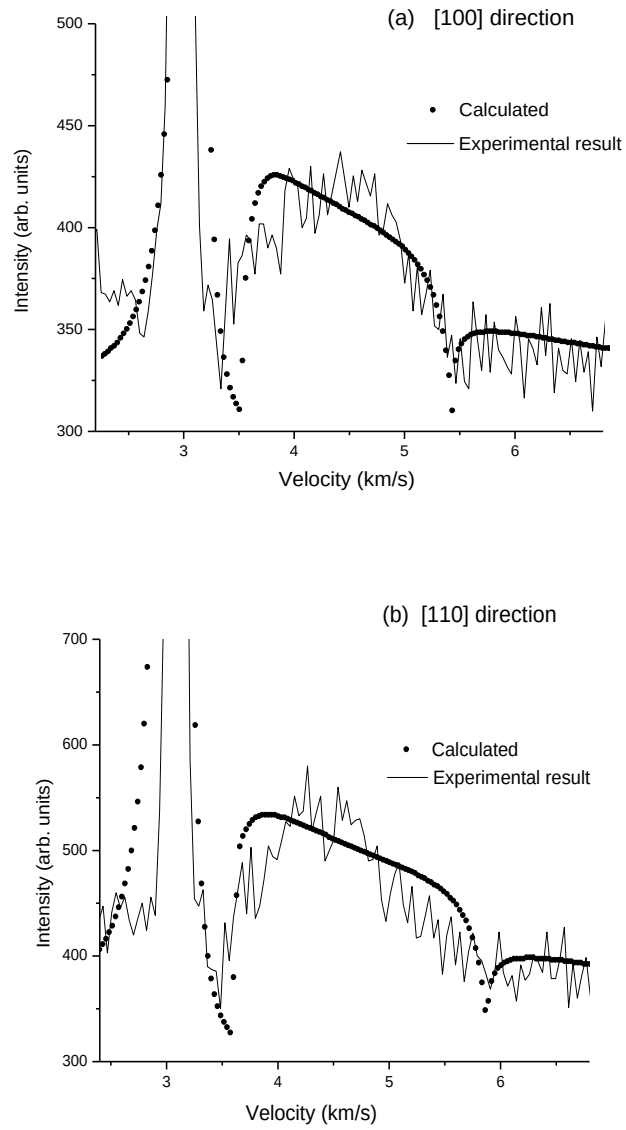


Figure 7.9: SBS spectra compared to calculated spectra for [100] and [110] surface wave directions ($\alpha = 0^\circ$ for the [100] direction in (a) and $\alpha = 45^\circ$ for the [110] direction in (b)) on the (001) plane surface of Rh_3Nb .

Using these elastic stiffnesses, SBS spectra in [100] and [110] directions were calculated (using Green's function methods) and compared to the measured spectra as shown in figure 7.9 (a) and (b). These show that there is satisfactory agreement between the measured and calculated SBS spectra in each of the wavevector directions.

7.4.2 χ^2 minimization of the secular functions

A simpler and more robust fitting procedure using the SBS measurements of and secular equations for the RSAW, LW and the Lamb shoulder threshold velocities in the [100] and [110] directions on the (001) surface of a cubic crystal can be used to determine the three elastic stiffnesses. The procedure is described in detail by Every *et al.*, (2010) and Kotane *et al.*, (2011).

This approach avoids the necessity of solving the cubic equations for the RSAW and p-SAW, instead it uses the merit function

$$\chi^2 = (h_1^2 + h_2^2) + w(h_3^2 + h_4^2), \quad (7.05)$$

where w is the relative weighting factor for the LW threshold velocities as compared to the RSAW velocities. In the [100] direction, the secular functions h_1 and h_3 that determine the surface and LW threshold speeds are given by equations (7.06) and (7.07), respectively. In the [110] direction, the corresponding secular equations for the wave speeds are h_2 and h_4 and are given by equations (7.08) and (7.09), respectively.

$$h_1 = \rho V_{RSAW}^2 - \left(\frac{C_{11}}{C_{44}} \times \frac{C_{44} - \rho V_{RSAW}^2}{C_{11} - \rho V_{RSAW}^2} \right)^{\frac{1}{2}} \times \left(C_{11} - \frac{C_{12}^2}{C_{11}} - \rho V_{RSAW}^2 \right) \quad (7.06)$$

$$h_3 = \rho V_L^2 - C_{11} \quad (7.07)$$

$$h_2 = \rho V_{RSAW}^2 - \left\{ \frac{C_{11}}{C_{44}} \times \frac{C_{44} - \rho V_{RSAW}^2}{\left[\frac{1}{2}(C_{11} + C_{12} + 2C_{44}) \right] - \rho V_{RSAW}^2} \right\}^{\frac{1}{2}} \times \left[\frac{1}{2}(C_{11} + C_{12} + 2C_{44}) - \frac{C_{12}^2}{C_{11}} - \rho V_{RSAW}^2 \right] \quad (7.08)$$

$$h_4 = \rho V_L^2 - \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) \quad (7.09)$$

All the secular functions must be zero to obtain a perfect fit. The weighting factor w assigned to the LW threshold velocities was set at 0.25 as discussed in Every *et al.*, (2010). This accounts for the associated features in the SBS spectra in figures 7.5 and 7.9 being less well defined and hence having greater measurement uncertainty. It is possible to obtain all three elastic stiffnesses from three equations (7.06, 7.07 and 7.08). Consequently the longitudinal wave threshold velocity in the [110] direction was not necessary for the fitting procedure (equation 7.09).

(a) Rh₃Zr

On minimisation of χ^2 the fitted values of the elastic stiffnesses of Rh₃Nb were found to be $C_{11} = 330$ GPa, $C_{12} = 188$ GPa and $C_{44} = 145$ GPa with $\chi^2 = 0.002$, $h_1 = -0.018$, $h_2 = 0.044$ and $h_3 = -0.018$.

(b) Rh₃Nb

On minimisation of χ^2 the fitted values of the elastic stiffnesses of Rh₃Nb were found to be $C_{11} = 369$ GPa, $C_{12} = 189$ GPa and $C_{44} = 162$ GPa with $\chi^2 = 0.001$, $h_1 = 0.030$, $h_2 = 0.014$ and $h_3 = -0.032$.

7.4.3 Discussion

The results of the two methods of extracting the elastic stiffnesses are presented in Table 7.1 for Rh₃Zr and Table 7.2 for Rh₃Nb.

Table 7.1: Elastic stiffnesses for Rh₃Zr using two different methods

Method	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
χ^2 minimization of modes	329	187	145
χ^2 minimization of the secular functions	330	188	145

Table 7.2: Elastic stiffnesses for Rh₃Nb using two different methods

Method	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
χ^2 minimization of modes	370	186	161
χ^2 minimization of the secular functions	369	189	162

In the present work two different methods have been used to obtain the elastic stiffnesses of Rh_3Nb and Rh_3Zr . The first method which we have named “ χ^2 minimization of modes” involves the extraction of elastic stiffnesses by the simultaneous fitting to the experimental results for the observed modes of surface wave velocity. The other method namely “ χ^2 minimization of the secular functions” uses the secular equations for the RSAW and LW threshold velocities in the [100] and [110] directions in an optimized fitting procedure to determine the three elastic stiffnesses C_{11} , C_{12} , and C_{44} . From Table 7.1 and Table 7.2 it can be concluded that there is good agreement between the two methods. The room temperature elastic stiffnesses of Rh_3Zr are $C_{11} = 329 \pm 2$ GPa, $C_{12} = 187 \pm 2$ GPa, $C_{44} = 145 \pm 1$ GPa, and those of Rh_3Nb are $C_{11} = 370 \pm 2$ GPa, $C_{12} = 187 \pm 3$ GPa, $C_{44} = 161 \pm 2$ GPa. The errors are tolerances in the minimization procedure.

Tables 7.3 and Table 7.4 show that the trend in the experimental results is consistent with the *ab initio* DFT calculations for the elastic stiffnesses of the two alloys. Thus the elastic stiffnesses of Rh_3Nb are higher than those of Rh_3Zr in both cases.

The elastic stiffnesses for both alloys are compared to the nickel-based alloys in Table 7.5. The elastic stiffnesses of both Rh_3Zr and Rh_3Nb are significantly higher than those of both a nickel based alloy (Ni_3Al) and nickel based superalloy (CMSX– 4). The retention of these excellent elastic properties at high temperatures would imply that the Rh-based alloys are potential candidates as base elements for new high and ultra high temperature alloys. These elastic stiffnesses determined by

the present study will be useful in thermodynamic calculations and in the determination of phase diagrams; these will be valuable in developing superalloys based on platinum group alloys.

Table 7.3: Comparison of experimental and calculated elastic stiffnesses for Rh₃Zr

Rh₃Zr	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)
This Work	329 ± 2	187 ± 2	145 ± 1
Chen <i>et al.</i> , 2004	300	150	133
Deviation	9%	20 %	8 %

Table 7.4: Comparison of experimental and calculated elastic stiffnesses for Rh₃Nb

Rh₃Nb	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)
This Work	370 ± 2	187 ± 3	161 ± 2
Chen <i>et al.</i> , 2004	395	172	175
Deviation	-7 %	8 %	-9 %

Table 7.5: Elastic stiffnesses for Rh₃Zr and Rh₃Nb compared to Ni₃Al

	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)
Rh₃Zr (This work)	329 ± 2	187 ± 2	145 ± 1
Rh₃Nb (This work)	370 ± 2	187 ± 3	161 ± 2
Ni₃Al (Frankel, 1986)	225	149	123
CMSX-4 (Zhang, 2001)	243	153	128

Conclusions and outlook

8.1 Summary of results

SBS is a useful non-contact technique for determining the elastic stiffnesses of both opaque thin supported films and bulk samples.

Prior to the experimental work and to demonstrate the effect of different substrates on the SBS spectra of a relatively high stiffness supported film, computational simulations were performed using surface Green's function methods. The simulated SBS spectra of TiC films on several substrates showed clearly the distinctions between a fast on slow (stiffening) system and a slow on fast (loading) system as well as between the strong and weak varieties of each category (stiffened and loaded). A discontinuity in the pseudo-SAW (pSAW) and pre-Rayleigh mode at some critical value of $q_{||}d$ was observed for the strong stiffening situation. However both the discontinuity and the pre-Rayleigh were not observed in a weak stiffening. In the case of slow on fast systems, film guided modes known as Sezawa waves (SW) whose displacement fields extend throughout the layer and decrease

exponentially with depth into the substrate were observed in addition to the Rayleigh SAW (RSAW). SW-like peaks known as pseudo-Sezawa waves (pSW) were only observed in the strong loading systems. These waves were more pronounced in the velocity region from the transonic state to the shear wave velocity of the substrate.

In all the simulations the elastic stiffnesses used for TiC films, $C_{11} = 492$ GPa, $C_{12} = 116$ GPa and $C_{44} = 188$ GPa, were calculated from single crystal elastic stiffnesses using the Voigt-Reuss-Hill averaging method. In practice these values proved higher than the film stiffnesses determined experimentally in the present study. In this context it is noted that Wittkowski *et al.* (2004) obtained elastic stiffnesses of tungsten carbide films (in the range 60 nm to 655 nm) which were almost half of those calculated using the Voigt-Reuss-Hill averaged approach, being a result similar to that of the present work on TiC. Pang (1998) reduced the bulk elastic stiffnesses by 25% to fit the dispersion curves for films less than 500 nm in thickness. It is considered that the complex microstructure of these transition metal carbides associated with the film growth conditions plays a major role in the variation of the elastic constants as compared with calculations with the Voigt-Reuss-Hill methods using single crystal data. Furthermore the lower mass density of 3.4 g/cm^3 determined for the TiC films used in the present work compared with the value of 4.9 g/cm^3 for a TiC single crystal obtained from literature (Petersen, 1982) is in accord with possible presence of microvoids. It can therefore be concluded that properties (density and stiffnesses) of thin layers ($d < 700$ nm) can be significantly lower than bulk elastic properties. In spite of the differences between the

calculations and the experiments, the former provided useful guidance in terms of the choice of different substrates to demonstrate the effects on the observed acoustic excitations of both stiffening and loading situations.

In the present work on thin supported films, the elastic stiffnesses for the TiC/Si and TiC/SiC systems were successfully determined from a least-squares fitting procedure of the velocity dispersion curves and used to simulate the respective SBS spectra. For each combination (*TiC/Si* and *TiC/SiC*), there is satisfactory agreement between measured and calculated SBS spectra. The discrepancies in the elastic stiffnesses between the two systems have been attributed to possible differences in the bonding of TiC films to silicon and silicon carbide.

It has also been established that elastic stiffnesses of films depend on the deposition conditions. The elastic stiffnesses increase with increasing applied RF power, over the measured range ≤ 250 W. For the negative substrate biasing of -70 V, there was an upward shift in the velocity dispersion curves which was attributed to the possibility of stress in the film or change in the micro-structure.

Platinum metal group alloys are promising candidates for future ultra-high temperature materials due to their excellent high-temperature properties. In this regard they are possible replacements for the Ni-based alloys which are predominantly used. It has been proposed that if the fcc and L1₂ coherent two phase structure is formed in an alloy with a higher melting temperature than that of Ni, then alloy would be stronger than Ni-based alloy (Yamabe-Mitarai *et al.*, 1997).

In the present work, two single crystal Rh-based alloys, namely Rh₃Zr and Rh₃Nb were studied by SBS. Two different approaches, “ χ^2 minimization of modes” and “ χ^2 minimization of the secular functions,” were used in the analysis of the SBS results to deduce the room temperature elastic stiffnesses of the Rh-based alloys from the experimental SBS spectra. The room temperature elastic stiffnesses of Rh₃Zr are $C_{11} = 329 \pm 2$ GPa, $C_{12} = 187 \pm 2$ GPa, $C_{44} = 145 \pm 1$ GPa, and those of Rh₃Nb are $C_{11} = 370 \pm 2$ GPa, $C_{12} = 187 \pm 3$ GPa, $C_{44} = 161 \pm 2$ GPa. To the best of our knowledge no experimentally measured elastic stiffnesses for Rh₃Zr and Rh₃Nb are available in the literature. However, the trend in the experimental results is consistent with the *ab initio* DFT (Chen *et al.*, 2004) calculations for the elastic stiffnesses of the two alloys. Thus the elastic stiffnesses of Rh₃Nb are higher than those of Rh₃Zr in both cases. The elastic stiffnesses of both Rh₃Zr and Rh₃Nb are significantly higher than those of a nickel based alloy (Ni₃Al).

8.2 Suggestions for future work

It has been established here that the SBS technique is sensitive to changes in micro-structure or composition of the films. Stress effects in the film were also observed as the deposition conditions were changed. As a result the technique has great potential for stress studies and for studying the effects of deposition conditions in thin films. Both aspects should be pursued in the future.

In terms of the elastic properties of thin supported films, only the weak fast on slow and slow on fast systems were examined in the present study. It will be

interesting to see how strong systems will behave experimentally. Strong slow on fast systems can be achieved for very hard thin films by using diamond as a substrate as proposed by Sumanya *et al.*, 2007. The behaviour of the elastic properties of hard films as a function of either temperature or pressure will be invaluable in their applications to industrial machining.

As for the bulk single crystal materials, Rh_3Zr and Rh_3Nb , future plans include determination of the high temperature elastic properties of these Rh-based alloys using a specially designed furnace. High temperature characteristics are important for the envisaged applications. Studies of variations of the elastic properties with pressure are also under consideration.

Chapter 9

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Publications

1. **Sumanya**, C., Comins, J. D., & Every, A. G. (2007). Surface Brillouin scattering in opaque thin films. *Journal of Physics: Conference Series* 92 012103.
2. **Jakata**, K., Wamwangi, D.M., Sumanya, C., Mathe, B.A., Erasmus, R.M., Naidoo, S.R., Comins, J.D. (2012). Thermally induced amorphous to crystalline transformation of argon ion bombarded GaAs studied with surface Brillouin and Raman scattering *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*
3. **Sumanya**, C., Mathe, B.M., Comins, J.D., Every, A.G., Osawa, M. and Harada, H. (2012). Room temperature elastic properties of Rh-based alloys studied by surface Brillouin scattering. *In preparation*
4. **Sumanya**, C., Wamwangi, D.M., Jakata, K., and Comins J.D., Surface Brillouin scattering study in TiC films. *In preparation*

Conference presentations

1. (July 2007) Surface Brillouin scattering studies in thin opaque films (Oral). 52nd South African Institute of Physics (SAIP), University of Witwatersrand, Johannesburg, South Africa
2. (July 2007) Surface Brillouin scattering in opaque thin films (Poster). 12th International Conference on Phonon Scattering of Condensed Matter. Paris, France

3. (May 2008) Surface Brillouin scattering in thin supported films (Oral). *1st African Laser Center (ALC) Student Symposium*. Kariega Reserve, Port Elizabeth, South Africa.
4. (July 2008) Elastic properties of platinum group alloys Rh₃Zr and Rh₃Nb using surface Brillouin scattering (Oral). *53rd South African Institute of Physics (SAIP)* University of Limpopo, South Africa. **Awarded the Most Outstanding Oral Presentation in the field of Condensed Matter Physics by a PhD student prize.**
5. (February 2010) Surface Brillouin scattering in thin films and bulk materials (Oral). *Academic Visit* Centre de Développement des Technologies Avancées (CDTA), Algeria
6. (April 2010) Room temperature elastic constants of platinum group alloys Rh₃Zr and Rh₃Nb using surface Brillouin scattering (Poster) *13th International Conference on Phonons Scattering 2010*, National Taiwan University, Taipei, Taiwan
7. (May 2010) *Academic Visit*. National Institute for Materials Science, Japan
8. (June 2010) Surface Brillouin scattering of bulk materials and thin supported films (Oral) *Material Research Physics Institute seminar* Physics Department, University of the Witwatersrand, Johannesburg.
9. (July 2011) Surface Brillouin scattering study of TiC thin hard films (Oral) *56th South African Institute of Physics (SAIP)* Physics Department, St George's Hotel, Pretoria, South Africa.
10. (April 2012) Elastic constants of platinum group Alloys (Rh₃Zr and Rh₃Nb) Using surface Brillouin scattering (Poster) *18th World Conference on Non-Destructive Testing* Durban, South Africa