High frequency organ-pipe modes in amorphous boron carbide observed using surface Brillouin scattering

B A Mathe1, J D Comins1 and A G Every2

1DST/CoE in Strong Materials, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa
2Materials Physics Research Institute, School of Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa

E-mail: matheb@science.pg.wits.ac.za

Abstract. Amorphous boron carbide films of 2 micron thickness were deposited at room temperature by a thermal deposition process on single-crystal silicon substrates. The elastic constants of an amorphous B4C film have been successfully measured by surface Brillouin scattering as a function of temperature, in the process, revealing a phase transition at about 350°C. Quantized wave-vector components perpendicular to the film surface associated with organ-pipe modes occurring within the film were used in conjunction with elastodynamic Green’s function calculations as well as independent measurement of longitudinal frequency from bulk excitations to extract the elastic constants.

1. Introduction
Boron carbide is the third hardest material at room temperature surpassed only by diamond and cubic boron nitride. It is also characterized by high thermal stability at elevated temperatures, and is the hardest known material above 1100°C [1,2]. The vibrational spectrum of the boron carbide film studied here includes resonances which originate from the presence of the interface between film and substrate: reflections of elastic waves in the film from the interface and from the film surface result in the formation of standing waves of longitudinal polarization in the direction of the surface normal, with nodes at the interface and antinodes at the surface. The wavelength is thus determined by the thickness of the B4C layer and the frequency is that of the corresponding longitudinal bulk phonons in the film. Additional information from the high frequency pseudo surface wave (HFPSAW) provides an independent validation of the elastic constants extracted using the Green’s function method.

2. Theoretical aspects
In Brillouin scattering photons are inelastically scattered by acoustic phonons. Considering a semi-infinite bulk, the mode localized at the surface of the half space and dominantly polarized parallel to the surface normal is known as the Rayleigh mode. In the case of a thin film supported on a substrate additional modes will appear, such as inner film modes due to reflections at the boundaries (Sezawa modes). For an opaque or semi-opaque medium, the light scattering is mediated principally by the surface ripple mechanism and involves interaction with surface excitations polarised in the sagittal plane, defined by the surface acoustic wave (SAW) propagation vector k_s and the surface normal. For homogeneous films it is found that the sound velocities of the localized modes only depend on the...
product of \( k \) and the film thickness \( d \) [3]. Therefore the dispersion of sound velocity is examined by varying the dimensionless product \( k/d \). In the first part of the experiment, \( k \) depends on the incidence angle \( \theta \) of light which is varied from \( \sin \theta = 0.5 \) to 0.95 (30 to 71°).

2.1. Experimental technique

A detailed description of the Brillouin scattering experimental set-up has been published elsewhere [4]. In brief, light from a Spectra Physics Ar\(^+\) laser with TM polarized \( \lambda = 514.5 \) nm line was focused onto the sample with an \( f/2.3 \) lens (\( f = 120 \) mm). The scattered light was collected with the same lens in a backscattered geometry and analysed using a high contrast and high-resolution tandem six-pass Fabry-Perot interferometer. The laser power incident on the sample was kept at about 5mW and each spectrum accumulated for at least 8 hours. The frequencies corresponding to each of the peaks were determined by a curve-fitting routine. The 2 micron thick film deposited on a silicon substrate had a density of 2 g/cm\(^3\)[8]. The dispersion investigation was conducted using a stage that allows for the variation of incidence angle, and during the process the scanning amplitude was also increased from 2.14 to 5.8 so as to be able to scan for high frequency modes. The phase velocity \( V_{\text{SAW}} \) of the SAW is given by \( \frac{\pi \Delta f}{k} \), where in backscattering geometry \( k = 2k_y \sin \theta \), with \( \Delta f \) corresponding to the measured frequency shift in the spectra. Figures 1 shows the SBS spectrum for B\(_4\)C measured at room showing the intense Rayleigh SAW and the low-intensity organ-pipe modes in the frequency regions 20 – 50 GHz.

As the incidence angle is increased, it is observed in figure 2 that mode frequencies occur in an approximately periodic manner. Moreover the finite frequencies of these modes increase further with increasing \( \theta \) and also do not disappear as \( \theta \rightarrow 0 \); such behaviour is in contrast to the normal Rayleigh surface waves. The local density of states at the free surface of the film \( D_i \) was evaluated within the Green’s function formalism \( D_i(\omega^2, K, x_3) = -\frac{1}{\pi} \text{Im} G_i(K, x_3, \omega^2) \), where \( i \) refers to the mode polarization; \( i = 1 \) for longitudinally polarized excitation, 2 and 3 respectively for shear and sagittal polarization normal to the surface and \( G_i \) the \((x_0, x_i)\) component of the Fourier domain elastodynamic Green’s function tensor for depth \( x_3 \). Thus calculations for \( D_i \) evaluated at the free surface are plotted and compared with experimental spectra in terms of the mode spacing. A small modification to the elastic constants for c-B\(_4\)C taken from literature [6,7,14,15] yields the best fit, namely at room temperature \( C_{11} = 396 \) GPa and \( C_{44} = 108 \) GPa for this amorphous B\(_4\)C film. These elastic constant values compare reasonably well with values quoted in ref. [12,14 and15] and when considering the experimental error (3 %).

2.2. Results and discussion

The periodicity of Brillouin peaks is traced to the constructive interference between ripple-mediated scattering amplitudes at the film boundaries. In contrast to the pioneering work by Zhang et al. [9,11], who worked with scattering angle \( \theta = 0 \) so as to measure photons backscattered essentially along the film normal, thus effectively probing only the \( k_z \) components of the acoustic excitations, we conducted our measurements starting at 30° incidence due to instrument-design constraints.
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The phase difference of the photons scattered from the two interfaces or film boundaries must be in exact quadrature for constructive interference to occur, otherwise there is suppression of alternate modes.

![Figure 1. SBS spectrum recorded at $\theta_i = 40^\circ$ incidence and using a scan amplitude of 2.14 at room temperature showing the organ pipe modes in the region from 20 GHz to about 60 GHz.](image1)

![Figure 2. SBS experimental data superimposed on a Green’s function calculated dispersion for boron carbide film plotted for the low-frequency region illustrated in figure 1 using the](image2)

![Figure 3. SBS spectrum recorded at $\theta_i = 71$ showing an additional SAW, namely HFPSAW that provides independent data for the $C_{11}$ value.](image3)
best-fit elastic constants.

In near-opaque materials, the scattering by bulk modes resulting from elasto-optic coupling is largely suppressed. However the high frequency pseudo-surface wave (HFPSAW) [16] results from a resonance where there is a corresponding peak in the surface power spectrum of the longitudinal modes. The HFPSAW can lead via elasto-optic coupling to a sharp peak in the Brillouin spectrum located such that \( \omega_{HFPSAW} = \omega_L \) for material having a Poisson ratio \( \sigma < 1/3 \). From the velocity of this wave (14.2 km/s) in figure 3 one computes the value of \( C_{11} \) to be 400 GPa which agrees very well with the value of 396 GPa extracted using the Green’s function methods.

3. Conclusions

Surface Brillouin scattering experiments were performed on an amorphous B₄C film and the elastic constants of amorphous B₄C film have been successfully measured at room temperature. Quantized wave-vector components perpendicular to the film surface associated with organ-pipe modes occurring within the film were used in conjunction with elastodynamic Green’s function calculations to extract the elastic constants which are found to be consistent with those obtained from the HFPSAW. This investigation has demonstrated that organ-pipe modes can be used to determine elastic properties of thin films provided the necessary conditions for their occurrence are satisfied by the specimen. The samples that were investigated were provided courtesy of Dr. T. Wittkowski of the University of Kaiserslautern, Germany.

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