Elastic properties of chalcogenide based phase change memories by surface Brillouin scattering

D Wamwangi[1,2]**, B Mathe**[1,2]**, M Baloi**[1]**, DG Billing**[3]**, C Persch**[4]**, M Salinga**[4] **and M Wuttig**[4]

[1] DST/NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa
[2] Materials Physics Research Institute, School of Physics, University of the Witwatersrand, Private Bag 3,WITS 2050, Johannesburg, South Africa
[3] School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, Republic of South Africa
[4] I. Physikalisches Institut 1A, RWTH Aachen University, 52056, Aachen, Germany

E-mail:daniel.wamwangi@wits.ac.za

Abstract. Chalcogenide based alloys continue to be intensively investigated as suitable candidates for universal non-volatile memory applications. This is driven by their fast and reversible phase transitions (ns) and their scalability potential. In this work the acoustic hardening of chalcogenide thin films on (100) Si is investigated to establish the bulk and shear modulus in the amorphous phase by surface Brillouin scattering. X-ray Reflectometry has been used to extract film thickness and density requisite parameters for simulation of velocity dispersion curves. Using surface Brillouin studies, phase change samples have shown the Rayleigh surface acoustic wave and higher order guided modes thus indicating a case of a slow on fast film-substrate configuration. The low surface roughness has been determined by X-ray Reflectometry to be less than 0.2 nm for all the films. Applying the elastodynamic surface Green function approach, c_{11} and c_{44} in the range 40-30 GPa and 15-10 GPa respectively were obtained.

1. Introduction

Phase change materials are chalcogenide compounds that have been used as the active medium in non-magnetic data storage [1]. Indeed their applications have varied between write once only memory (WORM), re-writable DVDs and the blue ray discs [2-3]. The concept of storage involves rapid and reversible change in optical and electronic properties using laser or current pulses. The ability to possess numerous storage (changes in resistance) states within a single cell has made them to be considered as potential candidates for highly scalable non-volatile memory devices. Their development as storage devices has been driven by their unique combination of properties such as rapid transformation (ns) between two structural states mediated by an electronic process, also known as threshold switching and stability against spontaneous recrystallization [4-5]. More recently these materials are being investigated for implementation as active medium in nanoelectromechanical systems (NEMS) and microelectromechanical (MEMS) systems due to their high potential for high

speed tunability of the mechanical properties and resonance frequency of the mechanical resonator [6]. This enables the development of lighter, scalable and low power mechanical resonators.

The phase change alloys that have been applied in optical storage comprise mainly of GeSbTe ternary alloys formed from the pseudo-binary tie line of GeTe and Sb_2Te_3 [2]. These alloys are also classified as nucleation dominated since their recrystallization occurs through the formation of critical nuclei through-out the volume of the bit. However there is also another class of phase materials in which phase transformation is dependent on the incubated nuclei at the amorphous and crystalline interface and the crystal growth speed towards the center of the bit. This latter class of materials is also called growth dominated phase change materials and can be easily scaled due to the linearity of the bit size with the laser or current pulse width. Despite the established research on these materials, their disordered state is not unique as the ensemble samples the potential energy landscape to minimize its internal energy with the driving force towards the metastable NaCl - like phase. These structural relaxations in the amorphous state have been attributed to the resistance drift in the phase change random access memories [7]. Thus, besides threshold switching, the thermal properties of phase change materials are crucial for not only the rapid and reversible switch but also for scalability purposes during resistive (joule) heating. Compared to the III –V counterparts, these materials have exceptionally low thermal conductivity even after the structural transition. Thermal conductivity of any material is determined by electronic and phonon transport in the medium and in this work we present the dynamics of the surface phonons in AgIn-Sb_2Te measured by surface Brillouin scattering to determine their elastic constants. The nature of the film - substrate configuration enables the investigation of near surface excitations which include Rayleigh surface acoustic wave (RSAWs), Sezawa waves (SW), pseudo–SAW and interface waves [8-9]. Using a Green's functions approach we determined the elastic properties of isotropic AgIn-Sb_2Te thin films from inverse problem of fitting the dispersion curves where the quality of fit was evaluated by overlaying the power spectrum to the measured surface Brillouin scattering spectrum.

2. Experimental

Thin films of AgIn-Sb_2Te have been grown on (001) Si using RF magnetron sputtering and evaluated for film thickness by X-ray Reflectometry (XRR). The XRR measurements have been performed using the Bruker AXS D8 Discover High resolution diffractometer. A highly collimated monochromatic Cu Kα X-ray beam operating at 1.6 kW in the symmetric geometry condition was used. The film thickness was determined to be 98 nm. Surface Brillouin scattering (SBS) measurements have been performed using a 335mW single mode laser light from a Torus Quantum 532 diode pumped solid state laser. The incident light was focused onto the surface of the film and the backscattered light was collected by a 120 mm focal length lens for frequency analysis using a high contrast Sandercock (3+3) pass Tandem Fabry-Pèrot interferometer [10]. The backscattered geometry was selected for maximum momentum transfer. Thus the incidence angle or film thickness can be varied to generate the surface phonon dispersion spectrum which is dependent on the ratio of the phonon wavelength relative to the film thickness [11]. The backscattering geometry is illustrated in Figure. 1, in which the wave vector of the surface phonons involved in the scattering process is obtained from momentum conservation of components parallel to the surface by the expression:

$$q_{II} = 2k_i sin\ \theta$$

(1)

Where $k_i \approx k_s$ is the incident wave vector and θ is the angle of incidence.
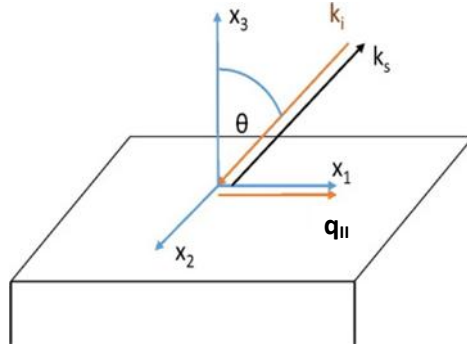
Figure 1. Backscattering geometry showing the propagation of the surface phonon due surface ripple mechanism.

The velocity v of the surface phonon modes for a ripple scattering mechanism is obtained from the frequency shift f as:

$$v = \frac{\pi f}{k_i \sin(\theta)}$$

(2)

In this project the film thickness of AgIn-Sb$_2$Te thin films was measured to be 98 nm while the incidence angle was varied between 51° and 70° to probe the dispersion of surface phonons in the range $1.8 \leq q_{II} d \leq 2.4$.

3. Results and Discussion

3.1. X-ray reflectivity of AgIn-Sb$_2$Te thin films

X-ray reflectometry was carried out on a 98 nm thin film of AgIn-Sb$_2$Te deposited on (001) Si, to determine the density and thickness of the film. Figure 2 shows the simulated and raw spectra overlaid on each other from which the density was obtained to be 6.45 ± 0.15 g cm^{-3} after fitting the critical angle ($2\theta = 0.63°$) for total external reflection. The film thickness of the layer was determined to be 98.00 ± 0.18 nm from the Kiessig oscillations using the layer stack, TeO$_2$/AgInSb$_2$Te/SiO$_2$/Si, while the exponential decay in the oscillations yielded an interfacial roughness of 0.20 ± 0.01 nm of the main layer.
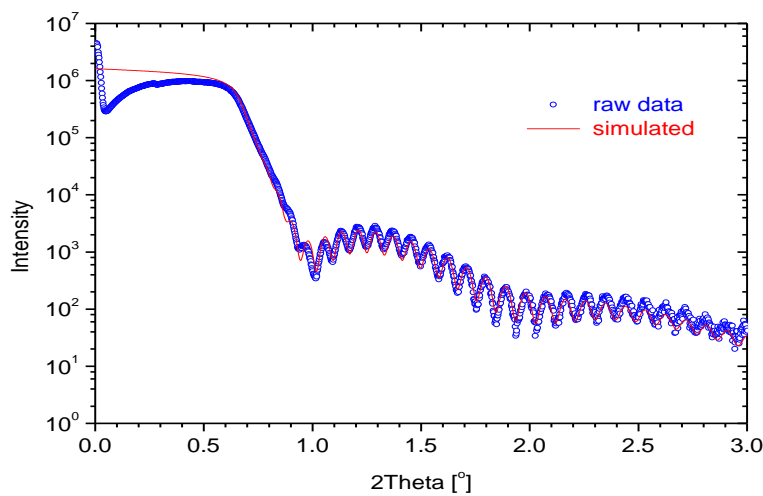

Figure 2. X-ray reflectivity spectra of the raw (blue circles) and simulated curves (red line) used to determine the mass density and thickness of the film.

An amorphous phase (not shown here) has been established in the layer using the Seemann-Bohlin geometry at a glancing incidence angle of 1.0° in omega. This confirms the presence of an isotropic film for which two effective elastic constants can be determined from the surface acoustic wave excitations.

3.2. Surface Brillouin scattering of phase change thin films on (001) Si.

Figure 3 shows a typical surface Brillouin scattering spectra collected for a 98 nm AgIn-Sb$_2$Te thin film on (001) Si substrate at various incidence angles. The spectra show 5 peaks in the frequency shift between 5 and 20 GHz. These peaks comprise of the most intense peak at 5 GHz corresponding to the true surface wave, known as the Rayleigh surface acoustic wave (RSAW). Notably, additional peaks at higher frequency shifts have been observed and they represent the high frequency guided modes (Sezawa Waves) which emerge from the reflections at the boundary. The presence of guided modes in the film is indicative of a case of slow on fast film - substrate configuration and these modes enable full determination of elastic constants of the phase change films.
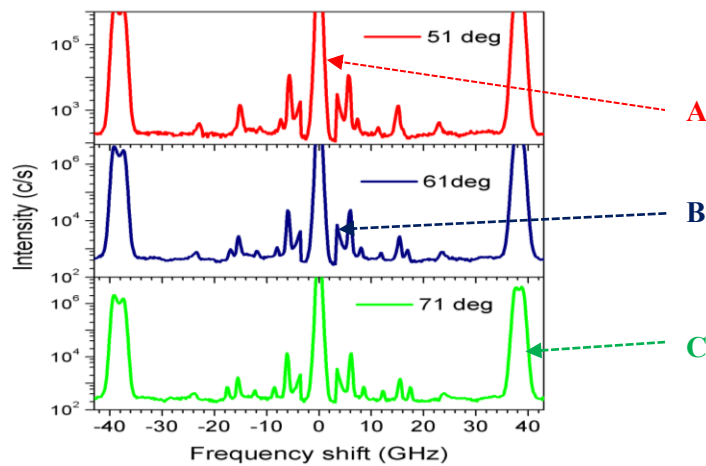

Figure 3. Surface Brillouin scattering spectra of AgIn-Sb$_2$Te thin film measured in backscattering geometry at 51°, 61° and 71° angle of incidence. The central peak A is an instrumental artefact related to the elastic light whilst B and C are instrumental effects related to alignment of the interferometer.

To determine the dispersive nature of the acoustic excitations, the velocity dispersion curve was plotted as shown (symbols) in figure 4[a] and fitted for the elastic constants using the surface elastodynamic Green's function approach (continuous function in the plot). As shown in figure 4(a), the velocity of the Rayleigh mode is asymptotic to 1500 m/s for large k_{II}d values. For this range of $k_{//}d$, the Rayleigh mode is not influenced by the properties of the substrate and the elastic constant determined is that of the film. On the other hand, as the film thickness approaches zero, the Rayleigh mode will approach to that of Si substrate at 4900m/s along [001] direction. Below this transverse threshold velocity, v_s^T, the dispersive nature of the Rayleigh and Sezawa waves (SW1,SW2 and SW3) is observed as shown in figure 4(a). The cross-sectional plot of figure 4 (b) shows a reasonably good agreement between the power and the experimental spectrum deviations in the spectrum intensity can arise due to reflections of the waves at the boundary.
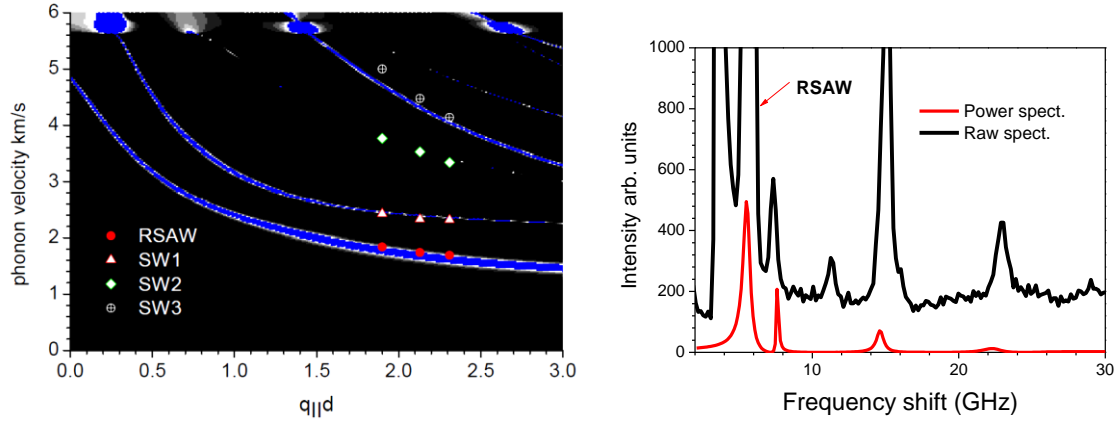
Figure 4. [a] Shows the computed Green's function velocity dispersion curve superimposed onto the discrete plot of the experimental data extracted from the spectra in Figure 3. [b] Cross-sectional plot ($k_{//}d = 2.3$) showing good agreement between the power spectrum derived from the Green's function and the experimental spectrum of the 98 nm film.

Included in figure 4[a] are the calculated dispersion curves of the discrete spectrum obtained from the least squares fitting to the experimental data using a combination of numerical solution of the wave equation and the surface elastodynamic Green's function approach [12-13]. This least-square fitting procedure allows for the inverse extraction of the thin film elastic constants. Since the phase change thin films are amorphous, hence elastically isotropic, two sets of effective elastic constants fully describe the system, and these have been determined from the best fit to be $C_{11} = 34.4 \pm 0.4$ GPa and $C_{44} = 14.3 \pm 0.3$ GPa respectively.

Using these values and the relation, $E = c_{11} - \frac{2c_{12}^2}{c_{11}+c_{12}}$ [12-14] yields the Young's modulus $E = 30.1$ GPa and a Poisson ratio, $\upsilon = 0.11$. The shear modulus of AgIn-Sb$_2$Te is equal to the C_{44} component of the elastic constant tensor. The values of the Young's Modulus are in the same range as those measured by Kalb ($E = 22.6$ GPa) and Blachowicz *et al* ($E = 24.5$ GPa, $v = 0.27$) [15 -16] using two independent techniques. The variation in the Poisson ratio could be attributed to the non-uniqueness of the disordered state of these materials.

4. Conclusion

In this work, surface Brillouin scattering technique has demonstrated the presence of and dispersive nature of high order resonances in the chalcogenide compounds, in addition to the Rayleigh surface acoustic wave (RSAW). The Rayleigh velocity has been determined to 1837 m/s which is much lower than that of Si (4800m/s), thus representing the case of a slow on fast film-substrate configuration. Using two effective elastic constants for an isotropic AgIn-Sb$_2$Te thin film, we successfully determined the room temperature Young's modulus (30.1 GPa), shear modulus (14.3 GPa), as well as the Poisson's ratio (0.11). The values are within range of reported literature values obtained using independent methods, thus demonstrating the versatility of the surface Brillouin scattering technique.

5. Acknowledgements

6. References

[1]   Feinleib J, deNeufville J, Moss S C and Ovshinsky S R 1971 *Appl. Phys. Lett.* **18** 254
[2]   Yamada N, Ohno E, Akahira N, Nishiuchi K, Nagata K and Takao M 1987 *Jpn. J.Appl. Phys.*

26 66

[3]   Wuttig M and Namada Y 2007 *Nat. Mat*. **6** 824

[4]   Raoux S, Welnic W and Lelmini D 2010 *Chem. Rev.***110** 240

[5]   Boniardi M, Redaelli A, Pirovano A, Tortorelli I and Pellizzer F 2009 *J. Appl. Phys.* **105** 084506

[6]   Nazeer H, Bhaskaran H, Woldering L A and Abelmann L 2015 *Thin Solid Films* **592** 69

[7]   Sebastian A Papandreou N, Pantazi A, Pozidis H and Eleftheriou E 2011 *J. Appl. Phys*. **110** 084505

[8]   Wittkowski T, Distler G, Jung K, Hillebrands B and Comins J D 2004 *Phys. Rev. B*. **69** 205401

[9]   Comins J D, Every A G, Stoddart P, Zhang X, Crowhurst J C and Hearne G 2000 *Ultrasonics* **38** 450.

[10]   Sandercock J R 1982 *Light Scattering in Solids III (*Berlin:Springer-Verlag)

[11]   Fioretto D, Carlotti G, Palmieri L, Socino G and Verdini L 1993 *et al., Phys. Rev. B*.**47** 15286

[12]   Every A G 2001 *Elastic properties of solids: static and dynamic principles. Handbook of Elastic properties of Solids, Liquids and Gases* vol 1, ed M Levy, H Bass and R Stern (New York: Academic Press)

[13]   Farnell G W 1970 *Physical Acoustics* ed W P Mason and R N Thurston (New York: Academic Press)

[14]   Nye J F 1972 *Physical Properties of Crystals* (Oxford: Oxford University Press)

[15]   Kalb J 2002 PhD thesis Aachen.

[16]   Blachowicz T, Beghi M G, Güntherodt G, Beschoten B, Dieker D and Wuttig M 2007 *J.Appl. Phys*. **102** 093519