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1995 J. Phys.: Condens. Matter 7 9147

(http://iopscience.iop.org/0953-8984/7/48/006)

J. Phys.: Condens. Matter 7 (1995) 9147–9153. Printed in the UK

Brillouin scattering determination of the whole set of elastic constants of a single transparent film of hexagonal symmetry

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Received 19 April 1995, in final form 14 July 1995

Abstract. In this work it is shown that the Brillouin light scattering technique can be successfully applied for determining the five effective elastic constants of a single transparent film of hexagonal symmetry, in the micron range of thicknesses. Measurements have been performed on a polycrystalline ZnO film, about 1.3 μm thick, supported by a Si substrate. A major result of this work is that the elastic constant c_{66} is selectively determined for the first time from detection of the shear horizontal mode travelling parallel to the film surface. Similarly, a selective determination of c_{11} is attained from observation of the longitudinal mode guided by the film. The three remaining elastic constants, namely c_{13}, c_{33} and c_{44}, can be then obtained from detection of the Rayleigh surface mode and of the longitudinal bulk wave propagating at different angles from the surface normal.

1. Introduction

The problem of the determination of the whole set of elastic constants of thin film materials has attracted much attention in recent years, because of the growing importance of layered structures in both theoretical studies and applications. In most practical cases one deals with polycrystalline films in the micron range of thicknesses, with a preferential orientation of the crystallites along the normal to the plane of the free surface. These films have a hexagonal (cylindrical) elastic symmetry which is characterized by five independent effective elastic constants. Measurement of the whole set of constants is usually out of the reach of conventional static techniques, which can only give information about specific elastic moduli [1]. On the other hand, use of acoustic techniques based on surface acoustic waves (SAW) presents technical difficulties connected with the fabrication of the acoustical delay line. In addition, one has to consider that in the frequency range commonly used, the large values of the acoustic wavelength, compared to the film thickness, require a careful consideration of the effect of the substrate on the propagation of the SAW [2].

An attractive experimental technique which has been affirmed in the last decade as a powerful non-destructive tool for the elastic characterization of thin films and layered structures is surface Brillouin scattering (SBS) [3]. It has many advantages over conventional ultrasonic techniques since it does not require external generation of acoustic waves and it probes acoustic phonons with wavelengths in the submicron range. In a SBS experiment, a beam of monochromatic light is used as a probe to reveal acoustic phonons which are naturally present in the medium under investigation. The power spectrum of these phonons is mapped out from frequency analysis of the light scattered within a solid angle, by means of a multipass Fabry–Perot interferometer. Most of the SBS investigations performed

0953-8984/95/489147+07$19.50

in the past for determining the elastic constants of thin films were concerned with layers of thicknesses lower than the acoustic wavelength (0.3–0.4 μm), supported by substrates with acoustic phase velocities higher than that of the films (slow film/fast substrate). Under these conditions, a number of discrete acoustic modes, namely the Rayleigh and the Sezawa modes [4], are revealed in Brillouin spectra and the corresponding phase velocity can be measured. These modes are dispersive, so that measurements are usually performed on films of different thicknesses and with different angles of incidence. In the case of films with hexagonal elastic symmetry and with the c axis of the crystallites perpendicular to the film surface, four of the five effective elastic constants, namely c_{11}, c_{13}, c_{33} and c_{44}, influence the Rayleigh and Sezawa modes, so that they can be evaluated by a best fit procedure of the experimental velocities to the calculated dispersion curves. Two main problems can limit the reliability of the above procedure. Firstly, the different elastic constants can influence the acoustic modes in a similar way, so that a strong correlation among the fitting parameters can occur [5]. Secondly, the best fit procedure relies upon measurements from films of different thicknesses (typically from 10 to 400 nm), neglecting possible structural and elastic differences among them. The fifth elastic constant c_{66} can be determined from measurement of the phase velocity of shear horizontal modes (Love modes). We notice, however, that since these modes are polarized parallel to the surface, their scattering efficiency is very low [6], so that the constant c_{66} has never been determined in a hexagonal transparent film [7].

The aim of this paper is to show that SBS can provide the amount of information necessary for an unambiguous determination of the whole set of independent elastic constants of a single transparent film of hexagonal symmetry, with thickness in the micron range. We have chosen to study ZnO films, because this material is extensively utilized in the field of surface acoustic waves, microwave acoustics and optoelectronics [8]. The elastic properties of sputtered ZnO films have been investigated in the past by SBS from both Rayleigh and Sezawa modes and by ultrasonics techniques [9–13]. In these previous studies large deviations of the measured elastic constants from those of the bulk material were observed, while more recently the improvement of deposition techniques made it possible to grow ZnO films with characteristics more similar to those of the bulk material [14]. We have chosen to use an opaque substrate (crystalline silicon) in order to take advantage of the presence of a reflecting interface which enhances the Brillouin cross section [15, 16]. Inelastic light scattering from both surface and bulk acoustic phonons enabled us to achieve a complete elastic characterization of the film material.

2. Experimental details

ZnO films, 1.3 μm thick, were deposited by RF reactive diode magnetron sputtering on (100) Si-substrates. The vacuum chamber was evacuated by a cryogenic pump to a background vacuum of about 10^{-7} Torr and a 10 min pre-sputtering was performed. The sputtering conditions were as follows: RF power 500 W; substrate temperature 225 °C; gas pressure and composition 3 mTorr of pure O_2; distance between Zn target and substrate 45 mm; growth rate 57 nm min^{-1}. X-ray diffraction experiments have shown that the films have a polycrystalline columnar texture with the c axis of the polycrystals oriented along the normal to the surface. Optical measurements performed using the prism-coupler method enabled us to determine the values of the ordinary ($n_0 = 1.975$) and extraordinary ($n_e = 2.053$) refractive indices.

Brillouin spectra were taken in air, at room temperature, using a 200 mW p-polarized light beam (single mode of the 514.5 nm line of an Ar^+ laser). The incident light was

focused onto the surface of the specimen and the back-scattered light collected by a lens with f number two and focal length 50 mm. The frequency analysis was performed using a Sandercock-type, 3 + 3 pass, tandem Fabry–Perot interferometer [3, 17], characterized by a finesse of about 100 and a contrast ratio higher than 5×10^{10}, the sampling time per spectrum was typically three hours.

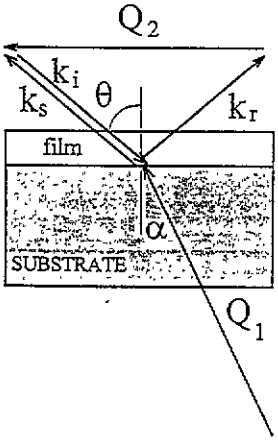

Figure 1. A schematic diagram of the interaction between photons and phonons, in the backscattering geometry. Here k_i, k_s and k_r are the wavevectors of incident, scattered and reflected photons, respectively, while Q_1 and Q_2 are those of bulk and surface phonons, respectively.

As stated before, the structure analysed, consisting of a transparent film on an opaque substrate, has been chosen in order to have a greater amount of information from a single spectrum. In fact, two different geometries of interaction contribute to the inelastic scattering of light from acoustic phonons in the film, as shown in figure 1. The first one relies upon direct coupling between incident photons of wavevector k_i and bulk acoustic phonons with wavevector

$$Q_1 = 2nk \tag{1}$$

where n is the refractive index of the film corresponding to the propagation direction of light. The second interaction geometry, which is allowed by the presence of both the free surface and the reflecting interface, involves acoustic phonons with wavevector:

$$Q_2 = 2k_i \sin(\theta) \tag{2}$$

parallel to the surface, where θ is the angle of incidence of light.

3. Results and discussion

Figure 2 shows a p–p spectrum taken at an angle of incidence $\theta = 70°$. The two well defined peaks at lower frequency, whose position has been shown to depend on θ according to equation (2), correspond to the Rayleigh surface wave (RW) and to the longitudinal mode (LM) travelling parallel to the film surface [18]. The latter has a longitudinal character and it is slightly leaky in the present case, because its phase velocity (about 6030 m s^{-1}) is larger than that of the transverse wave in the Si substrate. Measurement of the frequency

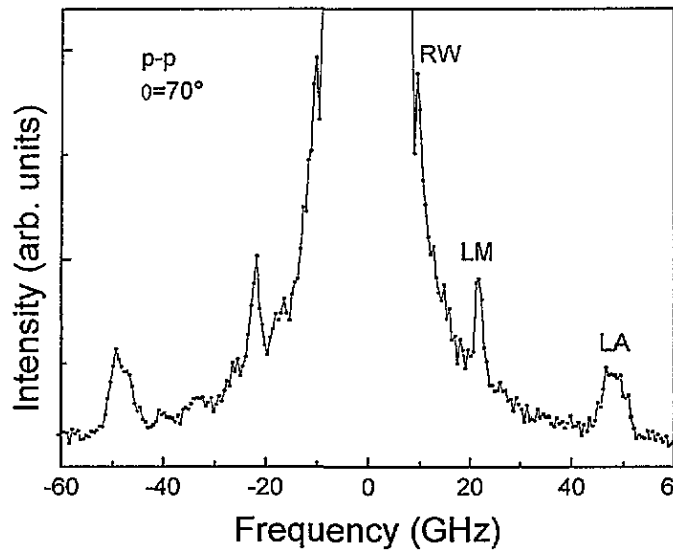

Figure 2. A p–p Brillouin spectrum taken at an angle of incidence $\theta = 70°$. RW, LM and LA indicate the peaks corresponding to: the Rayleigh wave; the longitudinal acoustic mode with wave vector parallel to the surface; and the longitudinal acoustic wave with wave vector at an angle of $\alpha = 28°$ from the surface normal.

position f of the Brillouin peaks enabled us to determine the phase velocity v of these acoustic modes, according to the equation:

$$v_2 = 2\pi f/Q_2 = \pi f/k_i \sin(\theta). \tag{3}$$

We notice that the phase velocity of the LM is $\sqrt{c_{11}/\rho}$, so that c_{11} could be selectively and directly evaluated. As for the RW, its velocity is $\beta\sqrt{c_{44}/\rho}$, where $\beta \cong 0.947$ is only weakly dependent on c_{11}, c_{13} and c_{33}. The third peak present on a larger frequency in the spectrum of figure 2 corresponds to the bulk longitudinal acoustic wave (LA). In contrast to the case of the previous two modes, the interaction geometry is that relative to the bulk phonons whose wave vector is expressed by equation (1). The phase velocity is therefore given by:

$$v_1 = 2\pi f/Q_1 = \pi f/nk. \tag{4}$$

We notice that the LA peak is slightly broadened because the interaction volume is limited by the finite thickness of the film [19]. Due to a refraction at the air/film interface, the bulk wave associated with the LA peak has a wave vector at an angle

$$\alpha = \sin^{-1}(\sin\theta/n) \tag{5}$$

from the surface normal. For $\alpha \cong 0°$ the LA phase velocity is simply $\sqrt{c_{33}/\rho}$, while for increasing α, it depends also on c_{11}, c_{13} and c_{44}. Measurements of the LA velocity were performed at almost orthogonal incidence ($\theta = 10°$ corresponding to $\alpha \cong 5°$) and at larger angles ($\theta = 45°$ and $70°$ corresponding to $\alpha \cong 21°$ and $28°$, respectively). The data points are plotted in figure 3, which also shows the curve obtained by a best fit procedure of

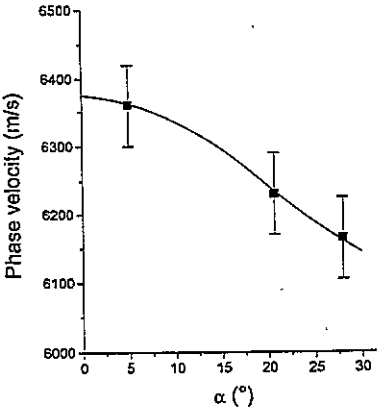

Figure 3. Experimental points of the phase velocity of the LA wave as a function of the angle of propagation from the surface normal. The solid curve is calculated by a best fit procedure, assuming the elastic constants to be free parameters.

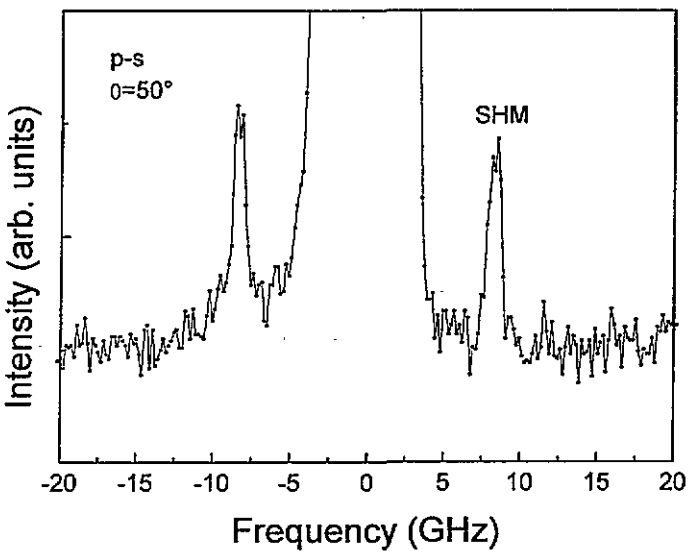

Figure 4. The p–s Brillouin spectrum taken at an angle of incidence $\theta = 50°$. The peak corresponding to the shear horizontal mode (SHM) with wave vectors parallel to the surface is clearly seen.

these experimental data, together with that of the RW, to the calculated phase velocities of the corresponding modes, assuming the constants c_{33}, c_{13}, and c_{44} to be free parameters. We notice that the piezoelectric character of the ZnO film has been taken into account by including piezoelectricity in the calculation of the phase velocities of the RW and LA modes, using the piezoelectric constants given in [20].

The last elastic constant to be determined is c_{66} which usually cannot be determined, as mentioned above, because of the very low scattering efficiency of Love modes. In the present case, however, thanks to the rather large interaction volume and to the presence of the reflecting interface, we could observe the shear horizontal mode (SHM) in p–s spectra, as shown in figure 4. Due to the large film thickness, this mode is a shear horizontal wave travelling parallel to the surface, so that its phase velocity is simply $\sqrt{c_{66}/\rho}$. This permitted us to make a direct evaluation of c_{66}. We emphasize that, to our knowledge, this is the first

selective determination of the elastic constant c_{66} of a transparent film, by detection of the shear horizontal guided mode.

Table 1. Experimental values of the phase velocity of the different acoustic modes.

v_{RW} (m s^{-1})	v_{LM} (m s^{-1})	v_{SHM} (m s^{-1})	v_{LA} (m s^{-1})
			6365 ± 60 (at $\alpha = 5°$)
2675 ± 20	6035 ± 50	2790 ± 20	6230 ± 60 (at $\alpha = 21°$)
			6180 ± 60 (at $\alpha = 28°$)

Table 2. Experimental values of the elastic constants of the ZnO film analysed in the present work. For comparison, the values of the elastic constants of the bulk material are also reported.

	c_{11} (GPa)	c_{13} (GPa)	c_{33} (GPa)	c_{44} (GPa)	c_{66} (GPa)
ZnO film (this work)	206 ± 4	118 ± 10	211 ± 4	44.3 ± 1	44.6 ± 1
Bulk material[a]	207–209	101–106	209–221	44.1–46.1	44.5–44.6

[a] From [20]. Minimum and maximum values are indicated.

The experimental values of the phase velocity of the different acoustic modes are reported in table 1, while the deduced elastic constants are shown in table 2. For comparison, we have also reported the values of the elastic constants of bulk ZnO. It can be seen that there is substantial agreement between the constants of the film and those of bulk ZnO, except for c_{13} which exhibits a moderate increase. This result shows that, in contrast to the large anomalies observed in the past [9–13], the ZnO film analysed here has elastic properties which are rather close to those of the bulk material. This behaviour, which is in agreement with recent results of measurements of SAW velocities [14], is to be attributed to the improvement of the growing conditions of sputtered ZnO films.

In conclusion, we have used surface Brillouin scattering to determine the five effective elastic constants of a transparent ZnO film in the micron range of thickness, which is typical of many applications. The elastic constants c_{11} and c_{66} where directly obtained from measurement of the phase velocity of the longitudinal mode and of the shear horizontal mode in the film material. The remaining constants, c_{13}, c_{33} and c_{44}, where evaluated from measurement of the phase velocity of the Rayleigh surface wave and of the longitudinal acoustic wave for different propagation directions. This demonstrates that Brillouin spectra from a single transparent film of about one micron thick can provide the amount of information necessary for the unambiguous determination of the whole set of independent elastic constants.

References

[1] Review articles can be found in 1992 *MRS Bulletin* vol XVII number 7 (Pittsburgh: Material Research Society) pp 25–45

[2] See for instance Coufal H, Meyer K, Grygier R K, de Vries M, Jenrich D and Hess P 1994 *Appl. Phys.* A 59 83

[3] Nizzoli F and Sandercock J R 1990 *Dynamical Properties of Solids* ed G K Horton and A A Maradudin (Amsterdam: North-Holland) vol 6 p 307
[4] Farnell G W and Adler E L 1972 *Physical Acoustics* ed W P Mason and R N Thurston (New York: Academic) vol 9 p 35
[5] Nizzoli F, Bhadra R, Lima O F, Brodsky M B and Grimsditch M 1988 *Phys. Rev.* B **37** 1007
[6] Recently observation of SH modes in the case of a buried SiO_2 film on silicon has been reported by Bottani C, Ghislotti G and Mutti P 1994 *J. Phys.: Condens. Matter* **6** L85
[7] SBS was used to measure the elastic constant c_{66} in Nb/Cu metallic superlattices, by detecting the tails of the acoustic modes in the sapphire substrate, see Bell J A, Zanoni R, Seaton C T, Stegeman G I, Bennet W R and Falco C M 1988 *Appl. Phys. Lett.* **52** 610
[8] Hickernell F S 1985 *IEEE Trans. Sonics Ultrason.* **SU-32** 621
[9] Hickernell F S 1973 *J. Appl. Phys.* **44** 1061
[10] Carlotti G, Socino G, Petri A and Verona E 1987 *Appl. Phys. Lett.* **51** 1889–91
[11] Carlotti G, Socino G and Verona E 1989 *J. Appl. Phys.* **65** 1370–2
[12] Carlotti G, Fioretto D, Palmieri L, Socino G, Verdini L and Verona E 1991 *IEEE Trans. Ultrason., Ferroelectr. Frequency Control* **38** 56–61
[13] Zhenxing Q, Xiaozhong Z, Mingzhon Z, Wizhong W and Yujin L 1985 *IEEE Trans. Sonics Ultrason.* **SU-32** 630
[14] Kim Y, Hunt W D, Hickernell F S and Higgins R J 1994 *J. Appl. Phys.* **75** 7299
[15] Carlotti G, Fioretto D, Palmieri L, Socino G, Anisimkin V I and Kotelyanskii I M 1993 *IEEE Ultrason. Symp. Proc.* (New York: IEEE) p 811
[16] Fioretto D, Carlotti G, Palmieri L, Socino G, Verdini L and Livi A 1993 *Phys. Rev.* B **47** 15 286
[17] A schematic diagram of the experimental apparatus can be found in Carlotti G, Fioretto D, Socino G, Verdini L and Pelosin V 1993 *J. Appl. Phys.* **73** 3028
[18] Lee S, Hillebrands B and Stegeman G I 1988 *J. Appl. Phys.* **63** 1914
Hillebrands B, Lee S, Stegeman G I, Cheng H, Potts J E and Nizzoli F 1988 *Phys. Rev. Lett.* **60** 832
[19] Doucet L and Carlotti G *Mater. Res. Soc. Proc.* vol 356 (Pittsburgh: MRS) at press
[20] Landolt-Bornstein 1979 *Numerical Data and Function Relationships in Sciences and Technology* (Berlin: Springer) Group III vol 11