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1997 J. Phys.: Condens. Matter 9 5575

(http://iopscience.iop.org/0953-8984/9/26/006)

J. Phys.: Condens. Matter **9** (1997) 5575–5580. Printed in the UK PII: S0953-8984(97)83438-8

Brillouin scattering study of epitaxial InSe films grown on the Si(111)1 × 1–H surface

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Received 15 April 1997

Abstract. Brillouin light scattering has been used to study the elastic properties of an InSe film grown epitaxially on a hydrogen-terminated non-reconstructed Si(111) surface. Both generalized Rayleigh–Sezawa and Love acoustic modes have been revealed, and their velocity dispersions measured as functions of the ratio between the film thickness and the acoustic wavelength. This enabled us to determine the complete set of InSe film elastic constants through a non-linear best-fitting procedure.

1. Introduction

It has been recently shown that layered materials having strong bonding only in two dimensions, such as InSe and GaSe, can be epitaxially grown on the hydrogen-terminated non-reconstructed Si(111) surface (Si(111)1 × 1–H), in spite of the presence of a very large lattice mismatch [1, 2]. This has triggered new interest in layered compounds, and many efforts have been made to gain better insight both into the process of this new kind of epitaxial growth, usually referred to as van der Waals epitaxy, and into the physical properties of the resulting systems [3–8]. In the case of InSe/Si(111)1 × 1–H, InSe is a semiconductor compound characterized by a layered structure with a single layer, about 0.8 nm thick, formed by four atomic planes in the sequence Se–In–In–Se. The bond between planes of the same layer is mainly of covalent type, with a small ionic contribution, while different layers interact predominantly via van der Waals forces. This happens because in these layers the covalent bonds are saturated, and therefore there are no dangling bonds on their surfaces, so these systems present a clear 'two-dimensional' character. On the InSe surface, Se atoms are arranged in a triangular lattice with hexagonal symmetry, where the distance between two adjacent Se atoms is 0.4 nm. The surface of the Si(111) substrate is, in contrast, a hexagonal-close-packed (hcp) lattice with a Si–Si distance of 0.384 nm. The 4% difference between the lattice parameters of the substrate and those of the film makes it impossible to obtain good heterostructures in a conventionally bonded heteroepitaxial system. To promote a van der Waals epitaxial growth on the Si(111) substrate, all of the surface dangling bonds are saturated with hydrogen atoms by wet chemical etching in basic HF solutions [9]. The resulting hydrogen-terminated non-reconstructed Si(111) surface is thus a very inert surface having a quasi-van der Waals nature, and, since it can be introduced

0953-8984/97/265575+06$19.50

into UHV without any hydrogen loss or contamination, a layered material may grow on such a surface through van der Waals interactions [2]. Previous studies of InSe crystals used Raman scattering to measure polar optical bulk phonons [10, 11], and thin InSe films epitaxially grown on Si(111) substrates have been characterized by Raman spectroscopy and reflection high-energy electron diffraction (RHEED) [12]. Films deposited at low substrate temperature ($T = 250$ °C) are reported to contain multiple domains oriented randomly, while at higher substrate temperature ($T = 300$ °C) the epitaxial films are monocrystalline. Recently, a study of the structural reconstructions and of the vibrational dynamics of thin InSe films on Si(111) has been carried out using helium atom scattering (HAS) [13, 8]. However, to our knowledge, no experimental investigation using long-wavelength acoustic phonons has been performed to study InSe films, and, consequently, no data are available concerning their elastic constants.

In this paper we report the results of an investigation of the elastic properties of InSe films, grown epitaxially on hydrogenated Si(111) 1×1 substrates. The experimental analysis has been performed using surface Brillouin scattering (SBS), which relies upon the inelastic scattering of light by thermally activated phonons [14]. This technique 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 the frequency analysis of the light scattered within a solid angle, by means of a multipass Fabry–Perot interferometer. In the presence of a substrate whose acoustic phase velocities are appreciably higher than that of the film (as in the case of InSe/Si), a number of discrete acoustic modes are revealed in Brillouin spectra, and the corresponding phase velocity can be measured for different angles of incidence. The values of these constants can be then obtained through finding the best fit of the experimental phase velocities to the calculated ones. In films with a hexagonal (cylindrical) elastic symmetry, a determination of the whole set of five elastic constants can be achieved by revealing both Rayleigh–Sezawa modes, polarized in the sagittal plane, and Love modes, with a shear horizontal (SH) polarization. The latter modes, however, cannot usually be revealed in thin transparent films, because of their low scattering efficiency [15]. In the present case, the high photoelastic coupling in the InSe film, together with the use of a reflecting film/substrate interface and the good performance of our interferometer, enabled us to reveal a Love-type mode, in addition to generalized Rayleigh–Sezawa modes. This made it possible to achieve a determination of all of the five independent elastic constants of the film.

2. Experimental procedure

Thin InSe films have been grown epitaxially, despite the 4% lattice mismatch, on a prototypical hydrogen-terminated non-reconstructed Si(111) substrate, using a conventional molecular beam epitaxy (MBE) system at a base pressure of about 1×10^{-10} Torr. Elemental In and Se were evaporated from Knudsen cells, and their fluxes monitored by a bare ion gauge placed on the manipulator. During the growth, the Si(111) substrate was held at a temperature of 360 °C, while the partial pressure ratio $R = P_{\mathrm{Se}}/P_{\mathrm{In}}$ was set to about 2.5, corresponding to a growth rate of 3.5 nm min^{-1}. InSe films with total thicknesses up to several tens of nm were grown. The MBE system is equipped with a 10 keV RHEED system operating at a grazing angle of about 1°. RHEED measurements, allowing us to monitor the quality of the Si substrate surface before the growth, as well as the structure of the InSe films during and after epitaxial growth, indicated a two-dimensional character of the InSe

films from the earliest stages (one monolayer). The epitaxial geometry deduced from the observed RHEED patterns is the following: (001) InSe ∥ (111) Si; [10$\bar{1}$0] InSe ∥ [1$\bar{1}$0] Si and [12$\bar{3}$0] InSe ∥ [11$\bar{2}$] Si.

Samples ($10 \times 10 \times 0.3$ mm^3) with films of thickness $h = 79 \pm 1$ nm (i.e. ≈100 InSe layers), as measured by an ellipsometric method, were kept in an inert nitrogen atmosphere during transportation from the Laboratoire de Physique de Solides (Université Pierre et Marie Curie, Paris, France), where they were prepared, to the Università di Perugia (Italy), where they were studied by performing BLS experiments.

Brillouin spectra were taken in air, at room temperature, using a 200 mW p-polarized light beam (a 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 2 and focal length 50 mm. The frequency analysis was performed using a Sandercock-type, $(3 + 3)$-pass, tandem Fabry–Perot interferometer [14, 16], characterized by a finesse of about 100, and a contrast ratio higher than 5×10^{10}. For measurements at incidence angles below 45°, we introduced a slit to limit the spread of the wavevectors of the collected light which would induce an appreciable broadening of the observed peaks; moreover, we increased the distance between the Fabry–Perot mirrors from 6 mm to 8 mm, in order to achieve a higher instrumental resolution. A polarization analyser was placed at the entrance of the interferometer in order to measure both polarized (p–p) spectra and depolarized (p–s) ones. For the former, typical acquisition times were of about half an hour, while for the latter, at least a couple of hours were needed.

As stated before, the structure analysed, consisting of a transparent film on an opaque substrate, permits a great amount of information to be obtained from a single spectrum, thanks to the cross-section enhancement caused by the presence of the reflecting interface. Because of the conservation of the momentum component parallel to the surface, the surface acoustic phonons involved in the scattering process have a wavevector whose modulus is [17]

$$Q_S = 2k_i \sin(\theta) \tag{1}$$

with k_i the modulus of the optical wavevector, and θ the angle of incidence of the light. Therefore, from measurement of the frequency position f of the Brillouin peaks, one can obtain the phase velocity v of the corresponding acoustic modes, according to the equation

$$v_S = 2\pi f/Q_S = \pi f/k_i \sin(\theta). \tag{2}$$

In our experiment, Q_S was parallel to the [1$\bar{1}$0] direction of the Si substrate. For this specific direction of propagation, the sagittal components of the displacements of the guided acoustic modes are not decoupled from the shear horizontal components. However, since this intercoupling depends on the symmetry of the substrate and not on the characteristics of the film itself, sagittal components predominate in some modes (Rayleigh–Sezawa-type modes) while the shear horizontal component predominates in others (Love-type modes).

3. Results and discussion

In order to study the dispersion of the phase velocity of guided acoustic modes as a function of the ratio between the film thickness and acoustic wavelength, we have performed SBS measurements at different angles of incidence, ranging from 70° to 15°, with 5° steps. A sequence of representative p–p spectra are shown in figure 1. The more intense peak, located at lower frequency (≈6–7 GHz), corresponds to the Rayleigh mode (R), while the second peak, labelled 'S', is due to the first Sezawa mode. The broadened structure visible

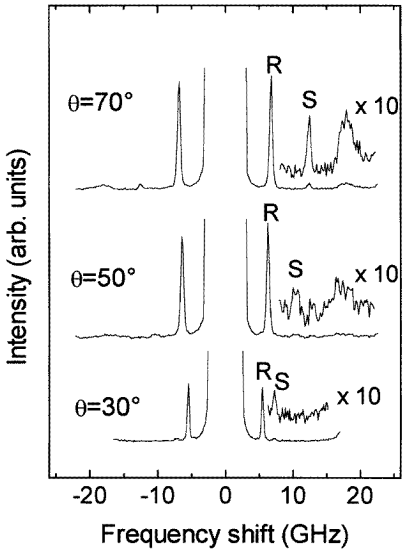

Figure 1. Brillouin spectra relative to a InSe film 79 nm thick, for three different angles of incidence. The peaks corresponding to the Rayleigh (R) and Sezawa (S) acoustic modes are clearly seen.

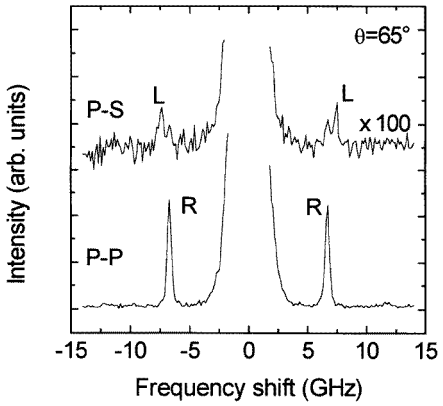

Figure 2. Brillouin spectra taken at an angle of incidence $\theta = 65^\circ$. The peaks corresponding to the Rayleigh wave (R) and to the Love mode (L) are clearly seen in the p–p spectrum and the p–s spectrum, respectively. Note that the ghost of the Rayleigh peak is also present in the p–s spectrum, because of the finite extinction ratio of the polarization analyser.

Table 1. Elastic constants of the InSe film determined by Brillouin light scattering. For the sake of comparison, the values of the constants of bulk InSe previously determined by ultrasonic techniques are also reported.

	c_{11} (GPa)	c_{33} (GPa)	c_{44} (GPa)	c_{12} (GPa)	c_{13} (GPa)
InSe film (this work)	68.4 ± 2.7	29.2 ± 0.7	6.27 ± 0.45	28.2 ± 3.2	12.2 ± 2.6
Bulk material, reference [19]	118.1	38.2	11.7	35.3	32
Bulk material, reference [20]	73	36	—	27	—

at higher frequency is due to a leaky mode which is located in the continuum part of the spectrum, i.e. above the threshold given by the value of the phase velocity of the transverse waves in the Si substrate (4680 m s^{-1}).

Measurements performed in the p–s configuration enabled us to observe also a Love-type mode (L), thanks to the efficient photoelastic coupling between light and the shear horizontal modes. A typical p–s spectrum is shown in figure 2, together with the corresponding p–p spectrum taken at the same incidence angle. It can be seen that, in spite of the rather weak signal-to-noise ratio, a well defined peak due to the L mode can be recognized. The weaker structure close to this peak represents the ghost of the R peak, whose presence can be attributed to the finite extinction ratio of the polarization analyser ($\approx 1/1000$). The detection of a Love-type mode is very important, since it gives us access to the determination

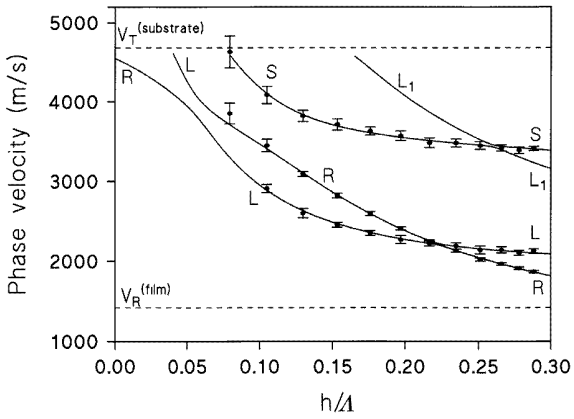

Figure 3. Experimental values of the phase velocity of the Rayleigh, Sezawa, and Love (L and L_1) acoustic modes (points with error bars) as functions of the ratio between the film thickness and the acoustic wavelength. The dispersion curves (solid lines) have been obtained from a best-fitting procedure, taking the elastic constants of the InSe film as free parameters.

of the complete set of InSe film elastic constants, including c_{12}, whose value is not usually determined in work concerned with hexagonal thin films. We have observed that the measured acoustic mode frequencies do not exhibit any appreciable dependence on the propagation direction on the film plane, at least for incidence angles larger than 45°, thus reflecting the cylindrical symmetry of the films. This experimental evidence, together with the fact that Rayleigh–Sezawa and Love modes appear only in p–p and in p–s spectra, respectively, confirms that, for the film thickness analysed, the observed modes present a well defined sagittal or shear horizontal character.

In figure 3, the experimental values of the phase velocity of the acoustic modes are plotted together with the dispersion curves calculated through a non-linear fitting procedure based on the Levenberg–Marquardt method, assuming the elastic constants to be free parameters, and with the mass density of InSe fixed at the value of $\rho = 5.51$ g cm^{-3} [18]. The data considered in the fit are those represented by the experimental points in figure 3; the value $\chi^2 = 6$ obtained in the fit is very good if one considers the 29 degrees of freedom.

The resulting values of the elastic constants are shown in the first row of table 1; the uncertainty reported for each constant takes into account both the experimental error and the statistical error related to the fitting procedure. For the sake of comparison, we have reported in the same table the constants of bulk InSe previously measured by two different groups, using ultrasonic techniques [19, 20]. We first notice that significant discrepancies appear between these two sets of bulk constants, especially in the values of c_{11} and c_{12}, whose origin could not be explained in the original papers. This prevented us from performing a quantitative comparison between the constants of the film and those of the bulk material. Anyway, we notice that, even though the film constants are, as a whole, lower than those of the bulk material, our results compare reasonably with the incomplete set of constants of reference [20]. On the other hand, remarkable differences are observed with respect to the constants given in reference [19]. In particular, the value of c_{13} quoted in reference [19] exceeds that determined by us far beyond the experimental error, yielding a ratio $c_{12}/c_{13} = 1.1$. This ratio, which is related to the elastic anisotropy, is instead $\approx$2.3 for our InSe film, a value rather close to that obtained for other lamellar compounds, such as GaS

(≈2.8) and GaSe (≈2.4) [20].

In conclusion, we have exploited surface Brillouin scattering to achieve the elastic characterization of epitaxial InSe films. This was accomplished by revealing both generalized Rayleigh–Sezawa acoustic modes and Love-type modes with a shear horizontal polarization. Measurement of the velocity dispersion of some of these modes yielded the information necessary for an unambiguous determination of the complete set of InSe film elastic constants through a non-linear best-fitting procedure. The results obtained show that the films are softer than the bulk material, even though a quantitative comparison is difficult, because remarkable discrepancies beset the two sets of constants currently available in the literature for bulk InSe.

Acknowledgment

LG received financial support from the Istituto Nazionale per la Fisica della Materia.

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and, in the second case, observation of SH modes in a buried SiO_2 film on silicon has been reported:
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while, more recently, the SH mode was detected in ZnO films 1 mm thick supported by a Si substrate:
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Carlotti G, Fioretto D, Socino G, Verdini L and Pelosin V 1993 *J. Appl. Phys.* **73** 3028
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