Elastic properties of GaSe films epitaxially grown on the Si(111)1 × 1-H surface, studied by Brillouin scattering

1999 J. Phys.: Condens. Matter 11 6661

(http://iopscience.iop.org/0953-8984/11/35/304)

J. Phys.: Condens. Matter **11** (1999) 6661–6668. Printed in the UK PII: S0953-8984(99)04159-4

Elastic properties of GaSe films epitaxially grown on the Si(111)1 × 1-H surface, studied by Brillouin scattering

V Panella†, G Carlotti†, G Socino†, L Giovannini‡, M Eddrief§ and C Sébenne§

† Unità INFM—Dipartimento di Fisica dell'Università, Via Pascoli, 06100 Perugia, Italy
‡ Unità INFM—Dipartimento di Fisica dell'Università, Via Paradiso 12, 44100 Ferrara, Italy
§ Laboratoire de Minéralogie Cristallographie, URA 9 at CNRS, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cédex 05, France

Received 10 May 1999

Abstract. Brillouin light scattering has been used to study the elastic properties of GaSe films of different thicknesses epitaxially grown on a hydrogen-terminated non-reconstructed Si(111) surface. Both Rayleigh and Sezawa guided acoustic modes have been revealed, and their velocity dispersion measured as a function of the ratio between the film thickness and the acoustic wavelength. This enabled us to determine four of the five GaSe film elastic constants through a non-linear best fit procedure. The fifth elastic constant c_{66} was obtained from detection of shear horizontal waves in the thicker film. The results obtained show that the film constants are similar to those of the bulk material, except for the shear elastic constant c_{44} which is appreciably lower. The values of the elastic constants thus obtained were used to calculate the Brillouin cross-section taking into account the rippling induced by surface phonons both at the free surface and at the interface. This permitted us to achieve a satisfactory reproduction of the experimental spectra.

1. Introduction

GaSe is a III–VI semiconductor compound with a layered crystalline structure. A single layer is about 0.8 nm thick and has two atomic planes of Ga sandwiched between two atomic planes of Se. Since the covalent bonds are saturated, there are no available dangling bonds at their surfaces, and therefore the layers are held together by van der Waals-like forces. For this reason this system is considered to have a 'two dimensional' character and many experimental and theoretical works have been devoted to the study of the vibrational as well as of the electronic properties of such layered materials [1]. Because of the weak forces between the layers that characterize this type of crystal, it is expected that the surface vibrational properties would be very similar to those in the bulk, as recently confirmed by bulk calculations and helium atom scattering measurements for GaSe and InSe [2, 3].

In a conventional chemically bonded heteroepitaxial system, it is often impossible to obtain good heterostructures because of lattice mismatch strain. This strain is largely reduced in van der Waals epitaxy by using materials which have strong bonding only in two dimensions [4–6]. It is also possible to promote such epitaxial growth on an Si(111) substrate having all the surface dangling bonds saturated with hydrogen atoms by wet chemical etching in HF solutions [7]. In fact, the hydrogen-terminated non-reconstructed Si(111) surface (Si(111)1 × 1-H) results in a very inert surface having 'quasi' van der Waals nature. Since it can be introduced into UHV without any hydrogen loss or contamination, it is an ideal substrate for growing

0953-8984/99/356661+08$30.00

a layered material which interacts with the surface only through van der Waals interactions [8]. The extension of such epitaxy on classical three dimensional substrates implies both atomic bonding and van der Waals interactions, and a lot of effort has been put into trying to understand the growth mechanism involved, i.e. how a two dimensional structure is bound to a three dimensional one. In order to answer this question, thin films of layered GaSe grown on different silicon(111) surfaces have been investigated using a variety of different techniques [9, 10]. In addition, thin GaSe films epitaxially grown on Si(111) substrates have been characterized by Raman spectroscopy and reflection high energy electron diffraction (RHEED) [11]. GaSe films deposited at low substrate temperature ($T_s \leqslant 400\,^{\circ}$C) are reported to contain multiple domains randomly oriented, while at higher temperatures ($T_s > 450\,^{\circ}$C) the epitaxial films are monocrystalline. The optical modes were found to be shifted towards the low frequency region with respect to the bulk. In spite of this experimental effort, no results concerning the elastic constants of these films are available in the literature to date.

The aim of the present work is therefore to fill the lack of experimental data on the elastic constants of GaSe films. Surface Brillouin scattering (SBS) has been exploited to study films of different thicknesses grown on the hydrogenated 1×1-Si(111) surface. SBS probes acoustic phonons with wavelengths in the submicron range, via the inelastic scattering of light by thermally activated phonons [12]. Since the acoustic phase velocities in the Si substrate are appreciably higher than that of the GaSe film, a number of discrete acoustic modes were detected in the Brillouin spectra, and the corresponding phase velocity could be measured for different incidence angles. The values of the elastic constants of the film have then been deduced from a non-linear best fit procedure. The obtained values of the elastic constants are compared with those previously reported for GaSe bulk single crystals [13, 14].

The rest of the paper is organized as follows: section 2 contains a description of the experimental procedure; section 3 deals with the results and the related discussion.

2. Experiment

Thin GaSe films are epitaxially grown, despite the 2.6% lattice mismatch, on the prototypical hydrogen terminated non-reconstructed Si(111) substrate using a conventional molecular beam epitaxy (MBE) 2300 Riber system with a background pressure, at room temperature, of about 10^{-10} Torr. In order to optimize the conditions leading to a van der Waals epitaxial growth, we saturate the Si(111) surface dangling bonds with hydrogen atoms by wet chemical etching in basic HF solutions [7]. The silicon wafers used are low n-doped (10^{15}–10^{16} cm^{-3}) 0.3 mm in thickness. Elemental Ga and Se were evaporated from Knudsen cells, and their fluxes monitored by a bare ion gauge placed onto the manipulator. Samples were then obtained by growing films of three different thicknesses. For all of them, during growth, the Si(111) substrate was held at a temperature of $T = 450\,^{\circ}$C, with the partial pressure ratio $R = (P_{Se}/P_{Ga}) = 6.5$, while the Ga partial pressure was set equal to 5×10^{-8} Torr, corresponding to a growth rate of 1.1 nm min^{-1}, for the two thinner films, and equal to 1.8×10^{-7} Torr, corresponding to a growth rate of 4.2 nm min^{-1}, for the thicker film. The respective thicknesses of the films were $h = 77.5 \pm 1$ nm (i.e. approximately 97 GaSe layers), $h = 251 \pm 4$ nm (i.e. approximately 314 GaSe layers) and $h = 990 \pm 10$ nm (i.e. approximately 1240 GaSe layers), as measured by an ellipsometric method.

The MBE system is equipped with a 10 keV reflection high energy electron diffraction (RHEED) system, which allows us to monitor the quality of the Si substrate surface before the growth, as well as the structure of the GaSe films during and after epitaxial growth. The grazing angle of the RHEED electron beam with the substrate is set to about 1°. RHEED measurements indicated a two-dimensional character of the GaSe film from the earliest stages

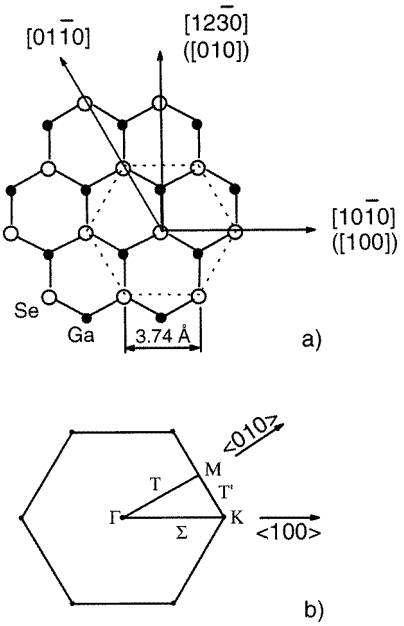

Figure 1. (a) Top view of the GaSe(001) surface structure showing the lattice vectors. The open circles are the Se atoms in the upper layer; the black circles are the Ga atoms in the lower layer. Two possible designations of the directions are represented. In parenthesis are the notations corresponding to the orthogonal unit vectors. The hexagonal unit cell is drawn with dashed lines. (b) The first Brillouin zone of the GaSe(001) surface. The high symmetry directions are displayed.

(one monolayer), and the observed RHEED patterns show that the (001) plane of the GaSe film is parallel to the Si(111) surface. Moreover the GaSe [10 − 10] azimuth is parallel to the Si [1 − 10] azimuth and the GaSe [12 − 30] azimuth is parallel to the Si [11 − 2] azimuth. Even though these are the correct notations to be used for the GaSe hexagonal structure, in the text the notations conventionally used for cubic crystals will be adopted, since such notations appear to be convenient to label the surface modes in layered crystals [15, 16]. Therefore, the [10 − 10] GaSe azimuthal direction will be denoted as [100] and the [12 − 30] direction as [010], i.e. in terms of the set of directions of equivalent axes, as ⟨100⟩ and ⟨010⟩ respectively. The top view of the GaSe(001) surface with the main directions is shown in figure 1(a), while figure 1(b) represents the corresponding first Brillouin zone with the high symmetry directions.

The samples ($9 \times 20 \times 0.3\ \mathrm{mm}^3$) were transported in an inert nitrogen atmosphere from the Laboratoire de Minéralogie Cristallographie (Université Pierre et Marie Curie, Paris, France), where they were prepared, to the University of Perugia (Italy) where they were studied by performing Brillouin light scattering experiments. Brillouin spectra were measured in air, at room temperature, by means of a 200 mW p-polarized light beam (an Ar^+ laser single mode of the 514.5 nm line). The incident light was focused onto the surface of the sample, and the backscattered light was collected by a lens having f-number 2 and focal length 50 mm. A Sandercock-type, (3 + 3)-pass, tandem Fabry–Pérot interferometer [12, 17], characterized by a finesse of about 100 and a contrast ratio higher than 5×10^{10}, was used to perform the frequency analysis. For measurements at angles of incidence below 50°, a slit was introduced in order to limit the spread of the wavevectors of the collected light and the Fabry–Pérot mirrors distance was increased from 6 to 8 mm in order to gain a higher instrumental resolution. A polarization

analyser, placed at the entrance of the interferometer, allowed us to measure both polarized (p–p) and depolarized (p–s) spectra with typical acquisition times of about half an hour and a couple of hours, respectively.

The surface acoustic phonons involved in the scattering process, thanks to the conservation of the momentum component parallel to the surface, have a wavevector whose modulus is equal to [18]:

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

with k_i the modulus of the optical wavevector and θ the angle of incidence of 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 $[1 - 21]$ direction of the Si substrate. For this specific direction of propagation, the sagittal components of the displacement of guided acoustic modes are decoupled from the shear horizontal components.

3. Results and discussion

In order to achieve a determination of the elastic constants of the GaSe films we studied the dispersion of the phase velocity of guided acoustic modes as a function of the ratio between film thickness and acoustic wavelength, performing SBS measurements at different angles of incidence, in the range between 40 and 70°. A sequence of representative p–p spectra corresponding to an incidence angle $\theta = 70°$, relative to each of the three GaSe films investigated is shown in figure 2. The more intense peak located at lower frequency, corresponds to the Rayleigh surface mode (R), while the other peaks labelled 'S' are due to the Sezawa modes which exist as guided modes below the threshold given by the value of the phase velocity of

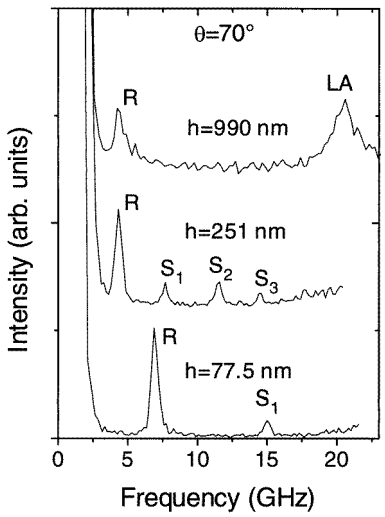

Figure 2. Brillouin spectra relative to the three GaSe films of different thickness h, for an angle of incidence $\theta = 70°$. The peaks corresponding to the Rayleigh (R) and Sezawa (S) guided acoustic modes are clearly seen. In the case of the thicker film, also the peak due to bulk longitudinal acoustic waves (LA) is observed.

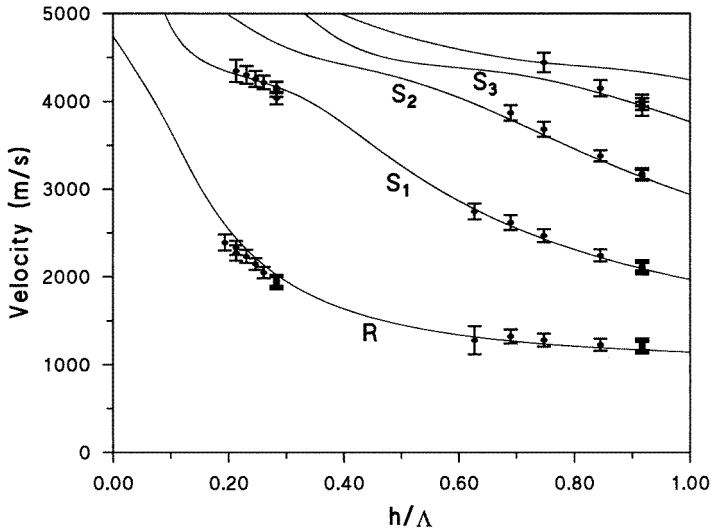

Figure 3. Experimental values of the phase velocity of the Rayleigh and Sezawa acoustic modes (points with error bars) as a function of the ratio between the film thickness and the acoustic wavelength. The dispersion curves (solid lines) have been obtained from a best fit procedure assuming the elastic constants of the InSe film as free parameters.

transverse waves in the Si substrate (about 5000 m s^{-1}). These modes are not clearly distinguished in the thicker specimens because they tend to form a continuous band of modes when the ratio between the film thickness h and the phonon wavelength Λ exceeds a few units. The broadened structure visible at higher frequency in the thicker film is due to the longitudinal bulk acoustic wave (LA). Its broadening is due to the limited thickness of the film if compared to the acoustic wavelength. In the case of films with elastic hexagonal symmetry four of the five effective elastic constants, namely c_{11}, c_{13}, c_{33}, and c_{44}, influence the Rayleigh and Sezawa modes. Therefore the phase velocities of the discrete Rayleigh–Sezawa modes (figure 3, points) have been measured and used to evaluate the values of the constants by a best fit procedure of the experimental velocities to the dispersion curves calculated through a non-linear fitting procedure based on the Levenberg–Marquardt method [19]. The mass density was kept fixed to the literature value $\rho = 5.03$ g cm^{-3}, while the four elastic constants c_{11}, c_{13}, c_{33}, and c_{44} were used as free parameters. We found, however, that the value of c_{13} could not be extracted reliably from our experimental data because it was affected by a large error (confidence limit). As a matter of fact, compared to the other constants, c_{13} influences the phase velocity of acoustic modes to a much lower extent. In addition, it is strongly correlated to the other fit parameters. For instance, a variation of c_{13} of 100% can be recovered by a change of the other elastic constants by only a few per cent. Therefore, in our final fitting procedure we fixed c_{13} to the value found in the literature for bulk GaSe [14]. We remark here the importance of evaluating the confidence limits on the fitted parameters, a point often underestimated: in our fitting procedure we have taken into account both the experimental error (error bars in figure 3) and the statistical dispersion of the experimental points. This is necessary in order to determine whether a given set of experimental data can determine unambiguously the fitted parameters, and to evaluate their reliability. Our results are shown in table 1, together with results from other works; the corresponding calculated dispersion relations are plotted in figure 3 (lines). The value $\chi^2 = 30.6$ we obtained, compared with the number of degrees of freedom (36), corresponds to a rather good fit.

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

	c_{11} (GPa)	c_{33} (GPa)	c_{44} (GPa)	c_{13} (GPa)	c_{66} (GPa)
GaSe film (this work)	96.1 ± 1.8	31.9 ± 0.7	5.41 ± 0.04	12.2[a]	37.5 ± 1.5
Bulk material [14]	105	35.7	10.5	12.2	38.8
Bulk material [14]	105	35.1	10.4	12.6	36.3

[a] c_{13} is kept fixed to the value in the bulk material.

In order to complete the evaluation of the elastic constants of the GaSe films, we tried to reveal shear horizontal modes, whose detection opens the way to knowledge of the fifth elastic constant, namely c_{66}. However, unlike the case of InSe films [21], measurements performed in the p–s configuration did not enable us to observe the Love-type mode in the two thinner films, probably because of a weaker photoelastic coupling between light and shear horizontal modes. Only in the case of the thicker film, $h = 991$ nm, was a very weak peak observed in p–s spectra for an incidence angle $\theta = 50^\circ$, whose origin could be attributed to shear horizontal modes propagating parallel to the film surface with a phase velocity $V_{SH} = 2730 \pm 50$ m s^{-1} which corresponds to $c_{66} = 37.5$ GPa, as reported in the table. In order to compare the physical properties of our films with those of the bulk material, we have reported in the same table the values of the elastic constants previously measured by BLS on bulk GaSe single crystals. It can be observed that, as a whole, the set of elastic constants of our films compare fairly well with those of bulk GaSe, except for the shear elastic constant c_{44}, whose value is mainly determined by the phase velocity of the Rayleigh wave at large values of the parameter h/Λ. This result is similar to those obtained in a number of artificially layered metallic systems, such as Nb/Cu, Mo/Ni, V/Ni, Mo/Ta, Ag/Ni, Au/Co and Ag/Co [20], where a marked decrease of the Rayleigh wave phase velocity v_R and of the shear effective elastic constant c_{44} has been observed for decreasing repetition periodicity. From the theoretical point of view, it has been shown that such softening can be connected with the presence of atomic disorder at the interfaces. With the exception of c_{44}, the GaSe film constants are rather similar to those we previously determined in the case of a similar system, namely InSe films epitaxially grown on the hydrogen-terminated non-reconstructed Si(111) surface [21]. This is in agreement with the fact that Raman and infrared reflection spectra [22] indicate that the interlayer interactions are rather similar for GaSe and InSe, the frequencies of the bulk vibrations being reproduced, to within 6%, by the same set of force constants.

As a final step of our investigation, we have used the obtained values of the elastic constants to calculate the acoustic displacement field in the GaSe films, in order to reproduce the measured Brillouin cross section. Because of the rather high value of the GaSe refractive index ($n = 3.07$), we have taken into account the ripple mechanism only, i.e. the light scattering caused by the corrugation of both the free surface and the film–substrate interface, while the photoelastic mechanism has been not considered. In our measurements the scattering is confined in the sagittal plane and, in addition, the normal modes in the sagittal plane, such as Rayleigh and Sezawa modes, are decoupled from shear horizontal modes. In this condition, the Brillouin cross section from surface ripples, which is proportional to the thermal-averaged mean-square displacements normal to the surface u_z, calculated at the free surface (0) and at the interface (h), can be written in backscattering geometry as [23]

$$I \propto |A(1 - \varepsilon^f)u_z(Q, \Omega; 0) + B(\varepsilon^f - \varepsilon^s)u_z(Q, \Omega; h)|^2 \tag{3}$$

where Ω is the acoustic frequency, ε^f and ε^s the dielectric constants of the film and

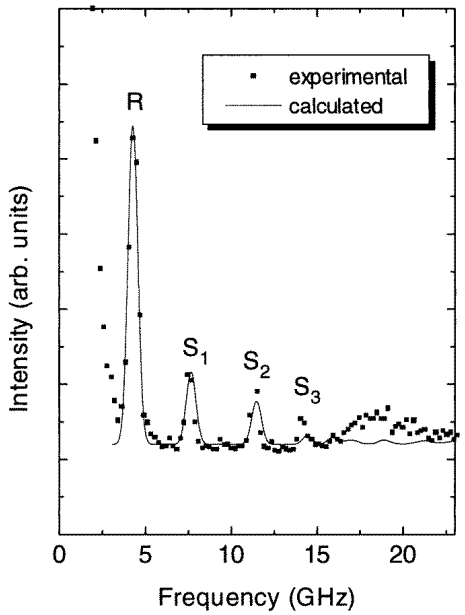

Figure 4. Comparison between the experimental spectrum (points) related to the GaSe film 251 nm thick and the theoretical spectrum calculated taking into account the rippling mechanism. The incidence angle of light is 70°.

substrate, while A and B are two terms whose cumbersome expression, involving scattering geometry parameters, is omitted here. Figure 4 shows a comparison between the spectrum measured in the 251 nm thick film for $\theta = 70°$, and the spectrum assuming the following values of the dielectric constants: $\varepsilon^f = 9.43$, $\varepsilon^s = 18.5 + 0.52\mathrm{i}$ [23]. The discrete Rayleigh and Sezawa modes have been convoluted with a Gaussian function of width $\Delta\nu = 0.6$ GHz, in order to reproduce the instrumental width. It can be seen that the agreement in both the position and the intensity of the discrete peaks is quite satisfactory, indicating that the rippling mechanism gives the main contribution to the scattering process. Only at frequencies above about 15 GHz does the calculated spectrum lie slightly below the measured one, probably because of the influence of the photoelastic effect which was not considered in our calculation. A fairly good comparison between the measured spectra and the calculated ones is also obtained for different incidence angles, and for the two thinner specimens.

In conclusion, we have exploited surface Brillouin scattering to achieve the first elastic characterization of epitaxial GaSe films grown on Si(111). Both the Rayleigh and up to three Sezawa guided acoustic modes were revealed in films of different thicknesses (77.5, 251 and 990 nm). Measurement of the velocity dispersion of these modes yielded the information necessary for a determination of four of the five GaSe film elastic constants through a non-linear best fit procedure. The fifth elastic constant c_{66} was obtained from detection of shear horizontal waves in the thicker film. The results obtained show that the film constants are similar to those of the bulk material, except for the shear elastic constant c_{44} which is appreciably lower. The values of the elastic constants thus obtained were used to calculate the Brillouin cross-section showing that it can be satisfactorily reproduced taking into account the surface and interface rippling mechanism.

Acknowledgments

Financial support from University of Perugia and from Istituto Nazionale per la Fisica della Materia is kindly acknowledged.

References

[1] See for example, Benedek G (ed) 1992 *Surface Properties of Layered Structures* (Dordrecht: Kluwer)
[2] Adler C, Honke R, Pavone P and Schroeder U 1998 *Phys. Rev.* B **57** 3726
[3] Panella V, Glebov A, Toennies J P, Sébenne C, Eckl C, Adler C, Pavone P and Schroeder U *Phys. Rev.* B at press
[4] Koma A and Yoshimura K 1986 *Surf. Sci.* **174** 556
[5] Saiki K, Ueno K, Shimida T and Koma A 1989 *J. Cryst. Growth* **95** 603
[6] Ueno K, Shimida T, Saiki K and Koma A 1990 *Appl. Phys. Lett.* **56** 327
[7] Higashi G S, Chabal Y J, Trucks G W and Raghavari K 1990 *Appl. Phys. Lett.* **56** 656
[8] Ueno K, Abe H, Saiki K and Koma A 1991 *Japan. J. Appl. Phys.* **30** L1352
[9] Reqqass H, Lacharme J-P, Sebénne C, Eddrief M and le Thanh V 1995 *Surf. Sci.* **331/333** 464
Reqqass H, Lacharme J-P, Sebénne C, M.Eddrief M and le Thanh V 1996 *Appl. Surf. Sci.* **92** 357
Reqqass H, Lacharme J-P, Sebénne C, Eddrief M, le Thanh V, Zheng Y L and Petroff J-F 1996 *Appl. Surf. Sci.* **104/105** 557
Koebel A, Zheng Y, Pétroff J F, Eddrief M, le Thanh V and Sébenne C 1995 *J. Cryst. Growth* **154** 269
[10] Faradev F E, Gasanly N M, Mavrin B N and Melnik N N 1978 *Phys. Status Solidi* b **85** 381
[11] Morhange J F, Jouanne M, Sacuto A, le Thanh Vinh, Eddrief M, Kanehisa M A, Ivanov I and Schwarcz R 1994 *The Physics of Semiconductors (Proc. 22nd Int. Conf.)* ed D J Lockwood (Singapore: World Scientific) p 297
[12] Nizzoli F and Sandercock J R 1990 *Dynamical Properties of Solids* vol 6, ed G K Horton and A A Maradudin (Amsterdam: North-Holland) p 297
[13] Chiang T C, Dumas J and Shen Y R 1978 *Solid State Commun.* **28** 173
[14] Gatulle M, Fisher M and Chevy A 1983 *Phys. Status Solidi* b **119** 327
[15] Brusdeylins G, Rechsteiner R, Skofronick J G, Toennies J P, Benedek G and Miglio L 1986 *Phys. Rev.* B **34** 902
[16] Benedek G, Hofmann F, Ruggerone P, Onida G and Miglio L 1994 *Surf. Sci. Rep.* **20** 1
[17] Carlotti G, Fioretto D, Socino G, Verdini L and Pelosin V 1993 *J. Appl. Phys.* **73** 3028
[18] Fioretto D, Carlotti G, Socino G, Modesti S, Cepek C, Giovannini L, Donzelli O and Nizzoli F 1995 *Phys. Rev.* B **52** R8707
[19] Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1992 *Numerical Recipes* (Cambridge: Cambridge University Press)
[20] Carlotti G, Fioretto D, Socino G, Hua Xia, An Hu and Jiang S S 1995 *Mater. Res. Soc. Proc.* **356** 385–90
[21] Panella V, Carlotti G, Socino G, Giovannini L, Eddrief M, Amimer K and Sébenne C 1997 *J. Phys.: Condens. Matter* **9** 5575
[22] Alieva L N, Blen'kii G L, Reshina I I, Salaev E Yu and Shteinshraiber V Ya 1979 *Sov. Phys.–Solid State* **21** 90
[23] Bortolani V, Marvin A M, Nizzoli F and Santoro G 1980 *J. Phys. C: Solid State Phys.* **16** 1757
[24] The value of the dielectric constant of the film was directly measured by an ellipsometric method, while its value for the Si substrate is taken from Bortolani V, Nizzoli F, Santoro G, and Sandercock J R 1982 *Phys. Rev.* B **25** 3442