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The elastic behaviour of finite-stage quasiperiodic Fibonacci a-Si:H/a-$Si_{1-x}C_x$:H multilayers

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Abstract. The Brillouin light scattering technique has been exploited in order to study the elastic properties of finite-stage a-Si:H/a-$Si_{1-x}C_x$:H semiconductor quasiperiodic Fibonacci multilayers, deposited by plasma enhanced chemical vapour deposition on crystalline silicon, fused quartz and corning glass substrates. Detection of the Rayleigh surface acoustic mode enabled us to study the evolution of the phase velocity of this mode as the number of Fibonacci stages is increased from eight to twelve and to evaluate the effective elastic constant c_{44}. The values obtained in these finite-stage Fibonacci structures are consistent with those calculated, by means of the effective modulus model, for an infinite quasiperiodic structure. In contrast to the anomalous elastic behaviour previously found in metallic superlattices, no elastic anomaly has been observed in the a-Si:H/a-$Si_{1-x}C_x$:H amorphous semiconductor multilayers, in agreement with recent theoretical models, which predict the presence of elastic anomalies in cases of symmetry difference and lattice mismatch between adjacent crystalline layers. Moreover, a slight decrease of the Rayleigh mode velocity has been observed on changing the substrate from c-Si to corning glass or fused quartz.

1. Introduction

Hydrogenated amorphous silicon carbide (a-$Si_{1-x}C_x$:H) has received great attenuation in recent years for both fundamental and applicative reasons. It is studied as a typical amorphous material with variable disorder [1] and used in relevant applications such as solar cells [2], optoelectronic devices [3], high-temperature coatings [4] and x-ray masks [5]. The most fascinating feature of this novel material is that a remarkable increase of material functions is obtained by controlling electrical, optical and photoelectronic properties, through adjustment of the atomic compositional ratio between Si and C [6, 7]. This has stimulated important developments in both the growth technology and the physical characterization of amorphous silicon carbide films, including extensive studies of their electrical, optical and structural properties [6, 8]. More recently, a-$Si_{1-x}C_x$:H/a-Si:H heterojunctions and multilayers have also been fabricated and their physical properties investigated experimentally [9, 10], as a natural extension of the effort devoted to the single constituent materials. To our knowledge, however, no detailed study of the elastic properties of this kind of structure has been performed to date.

In this paper we present the results of an investigation of the elastic properties of Fibonacci a-$Si_{1-x}C_x$:H/a-Si:H multilayers, deposited by plasma enhanced chemical vapour deposition (PECVD) on different substrates. These structures are an intermediate state

Table 1. Structural characteristics of the multilayers analysed, including the number of Fibonacci stages, the sublayer thicknesses d_A and d_B, the quasiperiodicity p_q and the total thickness h.

Sample	Number of Fibonacci stages	d_A (nm)	d_B (nm)	$p_q = \tau d_A + d_B$ (nm)	h (nm)
NSC8	eight	3.3	2.0	7.34	95.3
NSC11	eleven	3.3	2.0	7.34	405.7[a]
NSC12	twelve	3.3	2.0	7.34	653.2

[a] In this case an extra layer of a-Si:H, 2 nm thick, was added on top of the multilayer.

between periodic and random structures, since they present a quasiperiodic one-dimensional sequence along the growth direction. We have studied heterostructures with a finite number of Fibonacci stages, namely eight, eleven and twelve, since previous Raman studies of finite-stage Fibonacci multilayers have evidenced marked deviations from the ideal behaviour of an infinite Fibonacci lattice, even for a number of stages as large as ten [11]. The present study has been performed by means of the Brillouin light scattering technique, which permits detection of surface acoustic modes naturally present in the structure under investigation, in a wide range of acoustic wave numbers and angular frequencies [12]. Analysis of the frequency of these modes provides direct insight into the elastic properties of the multilayer and their dependence on the film thickness, substrate material and interface effects. Measurements performed on multilayers consisting of eight, eleven and twelve Fibonacci stages permitted us to test the suitability of a theoretical approach elaborated for an ideal Fibonacci sequence. The results obtained are discussed in light of the previous Brillouin spectroscopy studies of the elastic response of Fibonacci metallic multilayers, where the presence of elastic anomalies connected with the average density of the interfaces has been evidenced [13, 14].

2. Experimental details

The a-$Si_{1-x}C_x$:H/a-Si:H superlattices were grown on Si(001), fused quartz (SiO_2) and 7059 corning glass substrates using conventional PECVD in a capacitive RF glow discharge reactor. The deposition parameters were as follows: RF frequency, 13.56 MHz; RF power, 20 W; total work pressure, 300 mTorr and substrate temperature, 250 °C. The growth rate was 0.09 nm s^{-1} for the a-Si:H layers and 0.05 nm s^{-1} for the a-$Si_{1-x}C_x$:H ones. A gas mixture of CH_4 and SiH_4 was used, with a gas flow ratio $r = [CH_4]/([CH_4] + [SiH_4]) \cong 0.9$. From this value of r, the C fraction x has been estimated to be about 0.25, while the H content is about 30 at.%. It follows that the expected mass density of the a-$Si_{1-x}C_x$:H layers, calculated from the weighted average of those of a-Si (2.21 g cm^{-3}) and of a–C (1.2 g cm^{-3}), is about 1.96 g cm^{-3}. The Fibonacci structure consists of two building blocks A and B, with thickness d_A and d_B, which are superimposed according to the Fibonacci sequence $S_1 = A$, $S_2 = AB$, $S_3 = ABA$, $S_j = S_{j-1}S_{j-2}\ldots$ [15, 16]. The jth stage S_j consists of F_j elements A and F_{j-1} elements B, where F_j is the jth term of the Fibonacci series defined iteratively by the recurrent law $F_j = F_{j-1} + F_{j-2}$, for $j \geqslant 2$, with $F_0 = 0$ and $F_1 = 1$. When j increases, the ratio F_j/F_{j-1} converges to the irrational golden mean $\tau = (1 + \sqrt{5})/2 = 1.618\,03\ldots$. It follows that for high-generation multilayers the quasiperiodicity of the structures can be defined as $p_q = \tau d_A + d_B$. In the present case block A consists of 3.3 nm of a-Si:H, and block B consists of 2.0 nm of a-$Si_{1-x}C_x$:H, so $d_A = 3.3$ nm, $d_B = 2.0$ nm. We have studied three multilayers with eight, eleven and twelve stages, whose structural parameters are summarized in table 1.

Brillouin spectra were taken in air, at room temperature, using a 40 mW p-polarized light beam (single mode of the 514.5 nm line of an Ar^+ laser). The incident light was focused on the surface of the specimen and the back scattered light collected by means of 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 [12], characterized by a finesse of about 100 and a contrast ratio higher than 5×10^{10}; the sampling time per spectrum was typically 3 h. In the back scattering geometry used here, the wavevector $\boldsymbol{Q}$ of the surface phonons coming into the scattering process is

$$Q_{\text{surf}} = 2k_{\text{i}} \sin\theta \tag{1}$$

where k_{i} is the light wavevector and θ the angle of incidence; from this expression one can directly derive the connection between the frequency shift f of Brillouin peaks and the phase velocity v of the corresponding acoustic modes as follows: $v = \pi f / k \sin\theta$.

3. Theoretical background

Due to the conservation of momentum expressed by (1), surface acoustic phonons probed by Brillouin light scattering experiments have a wavelength comparable with that of light so the medium under investigation can be described within the framework of continuum elasticity. In the case of a multilayer with amorphous constituents, the elastic stiffness tensor has a cylindrical (or hexagonal) symmetry, with five independent effective elastic constants, namely c_{11}, c_{12}, c_{13}, c_{33} and c_{44}. The values of these constants in periodic structures can be calculated from those of the multilayer constituents, imposing the continuity of stress and strain across the interfaces, according to the procedure outlined in [17]. An extension of this procedure to the case of quasiperiodic structures has been introduced in [18], showing that a quasiperiodic structure with a large number of Fibonacci stages can be considered to be elastically equivalent to a periodic structure with sublayers A and B of thicknesses τd_{A} and d_{B}, respectively. In other words, one can define the relative fractions of blocks A and B as $f_{\text{A}} = \tau d_{\text{A}}/p_{\text{q}}$ and $f_{\text{B}} = d_{\text{B}}/p_{\text{q}}$. Therefore, its mass density can be written as

$$\rho = f_{\text{A}}\rho_{\text{A}} + f_{\text{B}}\rho_{\text{B}} \tag{2}$$

while its effective elastic constants can be derived from those of sublayers A and B simply by applying the effective modulus model to this equivalent periodic medium. For instance, the shear effective elastic constant of the multilayer can be expressed as

$$c_{44} = [f_{\text{A}}/c_{44}^{\text{A}} + f_{\text{B}}/c_{44}^{\text{B}}]^{-1}. \tag{3}$$

In the case of a Fibonacci structure consisting of a few stages above approach must be partially modified in the sense that the weighting factor τ in the expression of f_{A} and of the quasiperiodicity is no longer appropriate. In particular, for an n-stage multilayer, one has that the relative fractions of the elements A and B are $f_{\text{A}}^n = (F_{n-1}/F_{n-2})(d_{\text{A}}/d_n)$ and $f_{\text{B}}^n = (d_{\text{B}}/d_n)$ where d_n is the pseudo-quasiperiodicity, defined as $d_n = (F_{n-1}/F_{n-2})d_{\text{A}} + d_{\text{B}}$. These fraction values should be replaced in (2) and (3) in order to calculate the multilayer properties. We stress, however, that because of the rapid convergence of the Fibonacci series, the ratio F_{n-1}/F_{n-2} rapidly converges to τ when n increases, as shown in table 2, so that in the case of the a-Si:H/a-$Si_{1-x}C_x$:H multilayers analysed here, deviations of the elastic

Table 2. Values of the ratio between the number of blocks A and that of blocks B included in the nth Fibonacci stage S_n.

	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}
F_{n-1}/F_{n-2}	2.0	1.5	1.667	1.6	1.625	1.615	1.619	1.618	1.618	1.618

constants of the order of a few per cent from those of a semiinfinite Fibonacci structure are expected only in structures with less than five or six stages.

An experimental determination of the elastic constants of the multilayer films can be achieved from analysis of the surface phonon spectrum, revealed by Brillouin spectroscopy. This acoustic spectrum depends both on the ratio between total film thickness h and phonon wavelength Λ, and on the characteristics of the substrate material. In particular, for the specific structures analysed here, two different conditions can be distinguished, as follows:

(i) In the case of corning glass or fused quartz substrates, the transverse acoustic wave velocity in the film is higher than that in the substrate material, so only the Rayleigh acoustic mode can be supported, in a small range of values of h/Λ close to zero; for increasing film thicknesses this mode becomes leaky and degenerates in the pure Rayleigh wave of the film material for $h/\Lambda > 1$ [19].

(ii) In the case of the Si substrate, the transverse wave velocity in the film is lower than that in the substrate material, so a number of guided acoustic modes can be supported by the film, namely the Rayleigh and Sezawa modes, whose number increases with the ratio h/Λ. The phase velocity of these modes depends not only on the value of h/Λ, but also on the mass density and on the elastic constants of the film and of the Si substrate. However, for $h/\Lambda > 1$ one finds that the phase velocity of the Rayleigh mode depends almost exclusively on the value of the shear elastic constant c_{44} of the film and on its mass density [20].

4. Results and discussion

Figure 1 presents typical Brillouin spectra relating to two multilayers consisting of eight (NSC8) and twelve (NSC12) Fibonacci stages, supported by crystalline Si. The peak corresponding to the Rayleigh acoustic mode is clearly seen in these spectra. Due to the slow film–fast substrate combination, the Rayleigh mode undergoes dispersion with increasing number of Fibonacci stages, i.e. the ratio h/Λ, as reported in figure 2. In order to explain the experimental data quantitatively, we have also taken measurements on a-Si:H (element A of the multilayer), and a-$Si_{1-x}C_x$:H (element B of the multilayer) single films, about 0.5 μm thick, deposited on crystalline Si substrates. We could thus determine the values of the Rayleigh wave velocity in these films to be about 2820 m s^{-1} and 4180 m s^{-1}, respectively; from these values we estimated those of the shear effective elastic constants to be $c_{44}^{\text{a-Si:H}} = 45.3$ GPa and $c_{44}^{\text{a-Si}_{1-x}\text{C}_x\text{:H}} = 17.7$ GPa. Finally, the shear effective constant of the Fibonacci multilayer was evaluated through use of (3) to be $c_{44} = 31.8$ GPa. This expected value has then been used to calculate the dispersion of the phase velocity of the Rayleigh wave, which is plotted in figure 2 (dashed line), proving to be consistent with the experimental points relating to the three Fibonacci multilayers analysed.

A major result of the present work is therefore that the elastic properties of Fibonacci multilayers with eight, eleven and twelve stages do not exhibit any appreciable deviation from those expected for an infinite Fibonacci structure. In addition, in contrast to the anomalous behaviour of metallic quasiperiodic multilayers, such as Nb/Cu and Ta/Al

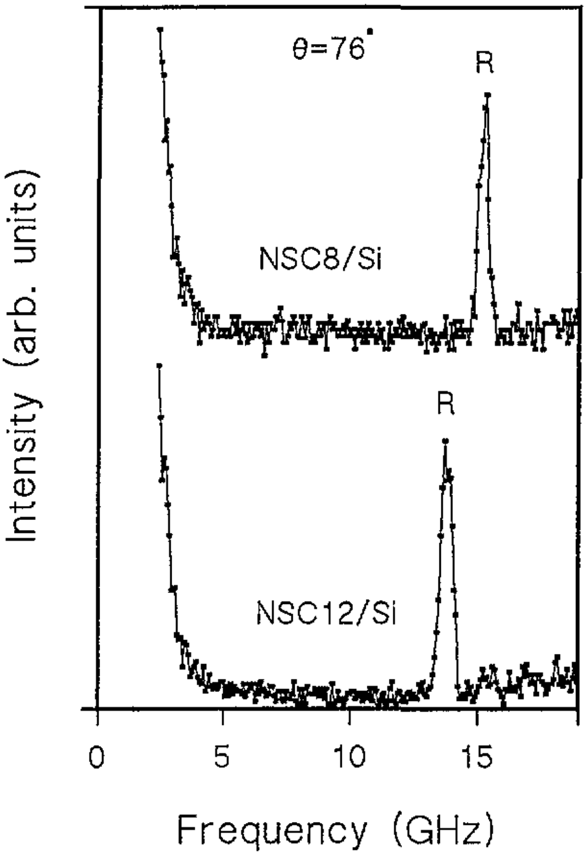

Figure 1. Brillouin spectra relative to two quasiperiodic multilayers with eight (NSC8) and twelve (NSC12) Fibonacci stages, deposited on silicon, for an angle of incidence $\theta = 76°$. The peak labelled R is due to the Rayleigh acoustic mode.

[13, 14], no elastic anomaly is found in the a-$Si_{1-x}C_x$:H/a-Si:H structures investigated. This ideal behaviour is similar to the one we have recently observed in a-$Si_{1-x}N_x$:H/a-Si:H multilayers, characterized by amorphous semiconductor constituents [18, 21]. In this respect we stress that the absence of elastic anomalies in semiconductor amorphous mulitlayers is consistent with the most recent theoretical models, which attribute the anomalous elastic behaviour of metallic structures to the lattice and symmetry mismatch between adjacent crystalline layers [22, 23].

We have also investigated the dependence of the elastic properties of the Fibonacci multilayers on the substrate material. Figure 3 presents three Brillouin spectra relating to the eleven-stage specimen deposited on three different substrates, namely corning glass 7059, fused quartz and (001) Si. It can be seen that the frequency position of the Rayleigh peak is somehow higher in the case of the Si substrate: in this case the phase velocity is about 3640 ± 30 m s^{-1} against the value of 3580 ± 30 m s^{-1} obtained for corning glass or fused quartz substrates. A similar result is also found in the case of the twelve-stage specimen. We notice that while in the case of the Si substrate the velocity of the Rayleigh mode starts from the substrate value of 4921 m s^{-1} and decreases for increasing h/Λ up to the Rayleigh velocity of the film, as shown in figure 2, in the case of fused quartz or corning

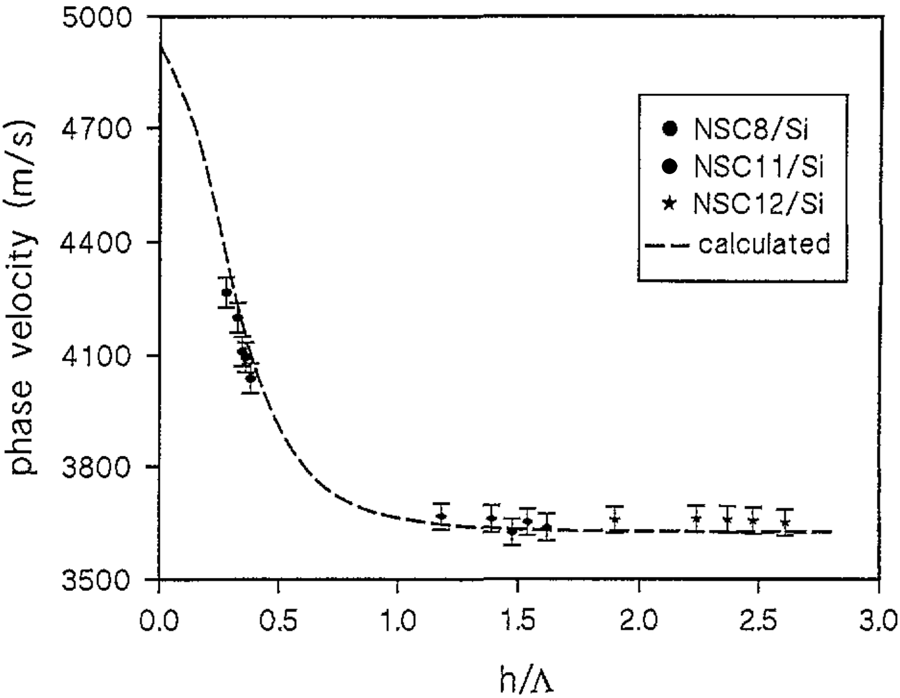

Figure 2. Experimental values (symbols) of the phase velocity of the Rayleigh mode on multilayers deposited on silicon, for different angles of incidence from 45° to 76°. The dashed line represents the calculated behaviour of the Rayleigh mode phase velocity assuming the value of c_{44} derived from measurements on a-Si:H and a-$Si_{1-x}C_x$:H single films.

glass substrates the velocity of this mode starts from 3600 and 3200 m s^{-1}, respectively, and then increases up to the Rayleigh velocity in the film (even if with a leaky character) [19]. For film thicknesses as large as about 0.5 μm, however, numerical simulation shows that this discrepancy, arising from the presence of different substrates, should be almost completely recovered and the values of the Rayleigh wave velocity calculated for Si, fused quartz and corning glass substrates coincide within 1 m s^{-1}. One can therefore reasonably hypothesize that the physical properties of the multilayer are affected by the substrate material in such a way that the Rayleigh wave velocity slightly decreases as the substrate changes from crystalline Si to fused quartz or corning glass. A similar dependence of the elastic properties of thin films on the characteristics of the substrate material, via interface effects, has been observed in previous Brillouin scattering studies [24].

5. Conclusion

The elastic properties of a-Si:H/a-$Si_{1-x}C_x$:H quasiperiodic semiconductor multilayers with eight, eleven and twelve Fibonacci stages have been investigated by means of the Brillouin light scattering technique. These multilayers are an intermediate state between periodic and random structures since they present a one-dimensional sequence along the growth direction that is quasiperiodic, i.e. characterized by two different fundamental periods whose ratio is irrational. Detection of the Rayleigh surface acoustic mode enabled us to study the evolution of the phase velocity of this mode as the number of Fibonacci stages is increased and to

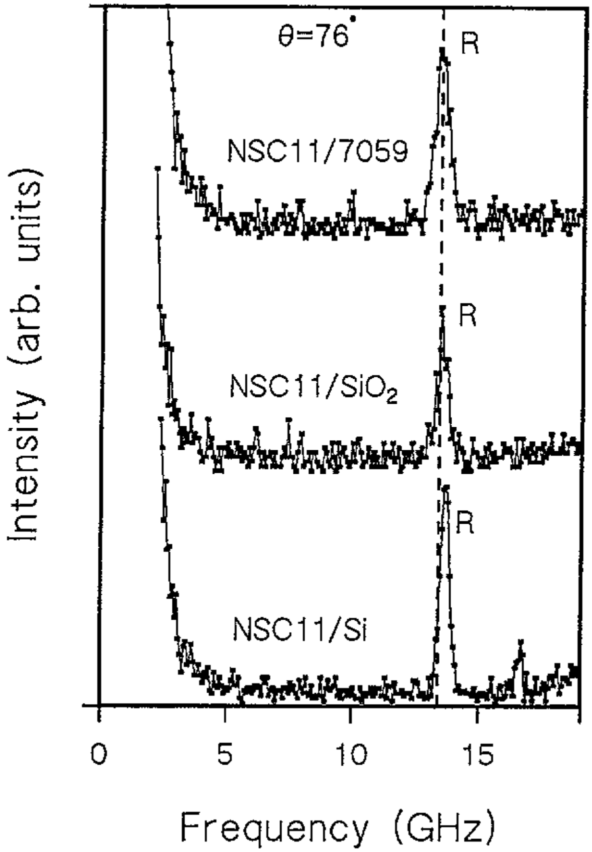

Figure 3. Brillouin spectra relative to the multilayer with eleven (NSC11) Fibonacci stages deposited on 7059 corning glass, fused quartz and Si, for an angle of incidence of 76°. The peak labelled R is due to the Rayleigh acoustic mode.

evaluate the shear effective elastic constant c_{44}. The expected value of this constant was calculated by means of the effective modulus model applied to quasiperiodic structures, using results of measurements of the elastic moduli of a-Si:H and a-$Si_{1-x}C_x$:H single films. This enabled us to show that the theoretical approach elaborated for calculating the elastic properties of an infinite Fibonacci sequence suitably apply to the case of finite-stage multilayers with eight generations or more. In addition, in contrast to previous Brillouin studies of the elastic response of Fibonacci multilayers with metallic constituents, there is a good agreement between the calculated values of the effective shear elastic constant c_{44} and those determined experimentally. This ideal behaviour of an amorphous layer structure is consistent with recent theoretical models which attribute the elastic anomalies observed in several metallic multilayers to atomic disorder caused by the lattice mismatch and the different symmetry of crystalline layers at the interfaces [22, 23]. Finally, a slight decrease of the Rayleigh velocity, probably associated with a modification of the residual stress in the multilayer film, has been observed as the substrate material is changed from crystalline Si to corning glass or fused quartz.

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References

[1] Pascarelli S, Boscherini F, Mobolio S and Evangelisti E 1992 *Phys. Rev.* B **45** 1650
[2] Schmidt M P, Solomon I, Tran-Quoc H and Bullot J 1985 *J. Non-Cryst Solids* **77/78** 849
[3] Tawada Y, Kondo M, Okamoto H and Hamakawa Y 1982 *Sol. Energy Mater.* **6** 299
[4] Sanders H J 1984 *Chem. Eng. News.* **62** 26
[5] Shimkunas A R, Mauger P E, Bourget L P, Post R S, Smith L, Davis R F, Wells G M, Cerrina F and McIntosh R B 1990 *J. Vac. Sci. Technol.* B **8** 1565
[6] Gat E, El Khankani M A, Chaker M, Jean A, Boily S, Pepin H, Kieffer J C, Durand J, Cros B, Rousseaux F and Gujrathi S 1992 *J. Mater. Res.* **7** 2478
[7] Hamakawa Y, Ma W and Okamoto H 1993 *MRS Bull.* **XVIII** 38
[8] Herremans H, Grevendonk W, van Swaaij R A C M M, van Sark W G J H M, Bernsten A J M, Arnold Bik W M and Bezemer J 1992 *Phil. Mag.* B **66** 787
[9] Yoshimoto M, Fuyuri T and Matsunami H 1989 *Phil. Mag.* B **60** 89
[10] Wang F, Fisher T, Muschik T and Schwartz R 1993 *Phil. Mag.* B **68** 737
[11] Aers G C, Dharma-wardana M W C, Schwartz G P and Bevk J 1989 *Phys. Rev.* B **68** 1092 and references therein
[12] Nizzoli F and Sandercock J R 1990 *Dynamical Properties of Solids* vol 6, G K Horton and A A Maradudin (Amsterdam: North-Holland) p 307
[13] Carlotti G, Fioretto D, Palmieri L, Socino G, Verdini L, Hua Xia, An Hu and Zhang X K 1992 *Phys. Rev.* B **46** 12 777
[14] Carlotti G, Socino G, An Hu, Hua Xia and Jiang S S 1994 *J. Appl. Phys.* **75** 3081
[15] Merlin R 1988 *IEE J. Quantum Electron.* **QE-24** 1791
[16] Dharma-wardana M W C, McDonald A H, Lockwood D J, Baribeau J M and Houghton D C 1987 *Phys. Rev. Lett.* **58** 1761
[17] Grimsditch M 1985 *Phys. Rev.* B **31** 6818
[18] Hua Xia, Zhang X K, Chen K J, Cheng G X, Feng D, Socino G, Palmieri L, Carlotti G and Fioretto D 1990 *Phys. Rev.* B **42** 11 288
[19] Farnell G W and Adler E L 1972 *Physical Acoustics* vol 9, ed W P Mason and R N Thurston (New York: Academic) p 35
[20] Carlotti G, Fioretto D, Socino G, Rodmacq B and Pelosin V 1992 *J. Appl. Phys.* **71** 4897
[21] Hua Xia, Carlotti G, Socino G, Chen K J, Zhang Wei, Li Z F and Zhang X K 1994 *J. Appl. Phys.* **75** 475
[22] Jaszczak J A, Phillipot S R and Wolf D 1990 *J. Appl. Phys.* **68** 4573
[23] Grimsditch M, Fullerton E E and Schuller I K 1993 *Mater. Res. Symp. Proc.* vol 308 (Pittsburgh PA: Materials Research Society) p 685
[24] Carlotti G, Fioretto D, Palmieri L, Socino G, Verdini L and Verona E 1991 *IEEE Trans. Ultrason. Ferroelectrics Freq. Control* **UFFC-38** 56