PHYSICAL REVIEW B VOLUME 44, NUMBER 16 15 OCTOBER 1991-II

Reflectivity studies of the strain dependence on E_0 and $E_0+\Delta_0$ excitonic transitions in ZnSe/GaAs

M. Stoehr
Laboratoire de Physicochimie des Matériaux Solides, Universitá Montpellier II,
place Eugene Bataillon, 34095 Montepellier CEDEX, France

F. Hamdani* and J. P. Lascaray
Groupe d'Etudes des Semiconducteurs, Université Montpellier II, place Eugene Bataillon,
34095 Montpellier CEDEX, France

M. Maurin
Laboratoire de Physicochimie des Matériaux Solides, Université Montpellier II,
place Eugene Bataillon, 34095 Montepellier CEDEX, France
(Received 2 April 1991)

The optical properties of ZnSe epilayers grown on (100) GaAs are greatly influenced by residual stress. Reflectance spectra of E_0 (light-hole and heavy-hole) and $E_0+\Delta_0$ excitonic transitions for layers thicker than 1 μm allow the determination of the ratio of the shear deformation potential (b) to the hydrostatic deformation potential (a). The value of the spin-orbit interaction (Δ_0) is also determined for each layer that suffers two-dimensional tensile stress due to the difference in the thermal-expansion coefficients. The polarization characteristics of excitonic transitions reveal the misorientation of the layer and allow unambiguous identification of the light-hole and heavy-hole excitonic transitions.

I. INTRODUCTION

The prospect of using ZnSe for visible-light-emitting devices and lasers with short wavelengths for display applications has caused a great deal of interest in producing high-quality material. The epitaxial growth of ZnSe on GaAs has been investigated extensively by use of molecular-beam epitaxy (MBE),[1-5] atomic-layer epitaxy (ALE),[1] hot-wall epitaxy (HWE),[5] and metalorganic vapor-phase epitaxy (MOVPE).[6-7] GaAs has been mostly used as a substrate for ZnSe epitaxial growth because of the small lattice mismatch of 0.27% at room temperature. Strain is created at the ZnSe/GaAs interface by the lattice mismatch and the different thermal-expansion coefficients of both compounds. Optical spectroscopy[1,2,6,8] has previously shown that ZnSe epilayers grow coherently on a (100) GaAs substrate with tetragonal compression up to a critical thickness of about 150 nm. With increasing layer thickness, a large density of dislocations,[9] which is formed near the interface, releases the strain. For epilayer thicknesses above 1 μm, it has been pointed out that the ZnSe epilayers suffer two-dimensional tensile stress due to the preponderance of the strain produced by the difference in the thermal contraction between ZnSe and GaAs on cooling below the growth temperature.

In this paper, heterostructures with ZnSe layer thicknesses ranging from 0.15 μm to 15 μm grown by MOVPE at the same substrate temperature, are investigated by reflectivity. The shift and splitting of the fourfold-degenerate valence band (Γ_8) to two doubly degenerate heavy-hole and light-hole bands and also the shift of the twofold-degenerate spin-orbit-split valence band (Γ_7) are observed and used to calculate the ratio of the deformation potentials (b/a). The effect of the linear polarization on the intensity of the excitonic transitions feature is also presented.

II. GROWTH AND EXPERIMENT

An atmospheric-pressure metalorganic vapor-phase epitaxy (MOVPE) system with a horizontal reactor was used for the epitaxial growth. A graphite susceptor was heated by rf induction coil. ZnSe epilayers with various thicknesses were grown on semi-insulating GaAs substrates oriented (100) ±0.5° off towards ⟨110⟩. The substrates were cleaned with a solvent, etched in a 4:1:1 solution of H_2SO_4 : H_2O_2 : H_2O, rinsed with deionized H_2O, dried with N_2, and loaded into the reactor. Prior to the growth, the substrates were thermally etched at 600 °C for 10 min in a hydrogen flow. Dimenthylzinc (DMZn) and diethylselenide (DESe) were used as source materials with molar flow rates of 28 and 92 μmol/min, respectively. The total hydrogen flow rate was 2 l/min. The growth was performed at 530 °C.

Standard reflectance technique is used to study excitonic transitions in the region of the band edge (4350–4550 Å) and in the region above the band edge (3750–3950 Å). Light from a tungsten lamp was focused on the epilayer surface at normal incidence. The samples were immersed in liquid helium. which is pumped below its λ point.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Effect of strain on the electronic band structure

For a zinc-blende-type material, the valence bands at the center of the Brillouin zone consist of a fourfold $P_{3/2}$ multiplet ($J=\frac{3}{2}$, $m_J=\pm\frac{3}{2},\pm\frac{1}{2}$) and a $P_{1/2}$ doublet ($J=\frac{1}{2}$, $m_J=\pm\frac{1}{2}$). Biaxial strain reduces the symmetry from T_d and thus splits the $P_{3/2}$ multiplet into an $m_J=\pm\frac{1}{2}$ (light-hole) and an $m_J=\pm\frac{3}{2}$ (heavy-hole) subband and also, because of the hydrostatic stress component of the strain, shifts the center of gravity of the $P_{3/2}$ multiplet and the $P_{1/2}$ doublet relative to the conduction band. The transitions between these valence bands and the lowest conduction band at $k=0$ are labeled $E_{\rm lh}$,$E_{\rm hh}$ and $E_0+\Delta_0$, respectively, where Δ_0 is the spin-orbit splitting of the valence bands at $k=0$. The energy change of the $J=\frac{3}{2}$ state and $\frac{1}{2}$ states relative to the conduction-band minimum induced by the strain can be found by calculating the strain Hamiltonian matrix using the unperturbed wave functions. The energy shifts with respect to its zero stress value for excitonic transitions associated with $\Gamma_6-\Gamma_8$ and $\Gamma_6-\Gamma_7$ band extrema are thus given by

$$\Delta E_{\rm lh}=\left[2a\frac{(C_{11}-C_{12})}{C_{11}}+b\frac{(C_{11}+2C_{12})}{C_{11}}\right]\epsilon\ , \tag{1}$$

$$\Delta E_{\rm hh}=\left[2a\frac{(C_{11}-C_{12})}{C_{11}}-b\frac{(C_{11}+2C_{12})}{C_{11}}\right]\epsilon\ , \tag{2}$$

$$\Delta(E_0+\Delta_0)=2a\frac{(C_{11}-C_{12})}{C_{11}}\epsilon\ , \tag{3}$$

where (C_{ij}) are the elastic stiffness constants of ZnSe,[10] a is the net hydrostatic deformation potential characterizing the relative energy shift of Γ_6 from valence bands (Γ_8 and Γ_7) under the hydrostatic component, b is the shear deformation potential of the valence bands, and $\epsilon=\epsilon_{xx}=\epsilon_{yy}=\epsilon_{\Delta a}+\epsilon_{\Delta\alpha}$ is the in-plane residual strain in the layer, which is the sum of two contributions [strain induced by the lattice mismatch ($\epsilon_{\Delta a}$) and thermal strain induced by the difference of the thermal contraction coefficients ($\epsilon_{\Delta\alpha}$)]. These equations are given under two approximations. The first is to neglect the stress-dependent spin-orbit Hamiltonian; then the spin-dependent deformation potential for hydrostatic effects is not taken into account.[11] As a consequence, the hydrostatic shift of the spin-orbit-split band is described by the hydrostatic deformation potential, which already described the hydrostatic shift of light- and heavy-hole bands.[12,13] Second, the shear component of strain induced in ZnSe epilayers is relatively small compared to the spin-orbit interaction and thus the coupling between sets of $m_J=\pm\frac{1}{2}$ bands (light-hole and spin-orbit-split bands) causing a nonlinear stress dependence of these transitions can be neglected.

Different combinations of these equations allow us to estimate the value of the ratio of the shear and hydrostatic deformation potentials as well as the spin-orbit splitting Δ_0. First, the value of the spin-orbit interaction is separately estimated[14] for each layer combining Eqs. (1)–(3),

$$\Delta_0=(E_0+\Delta_0)-\frac{E_{\rm hh}+E_{\rm lh}}{2}\ . \tag{4}$$

The stress splitting (δ) of the Γ_8 valence band is given by

$$\delta=E_{\rm lh}-E_{\rm hh}=\Delta E_{\rm lh}-\Delta E_{\rm hh}=2b\frac{(C_{11}+2C_{12})}{C_{11}}\epsilon\ . \tag{5}$$

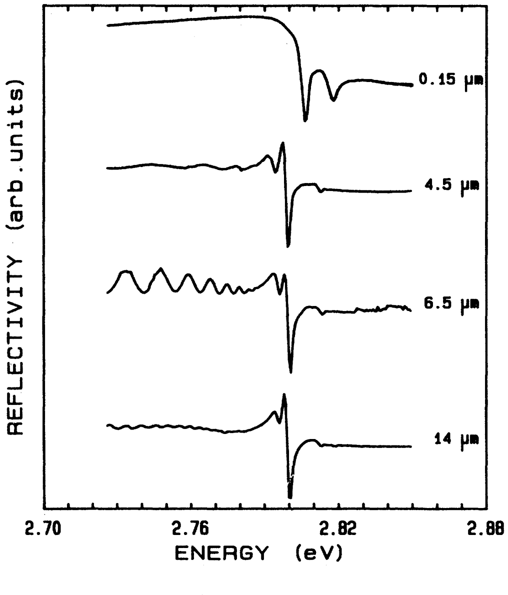

FIG. 1. Reflectivity spectra at 1.8 K of ZnSe epilayers grown on GaAs (100) for different thicknesses.

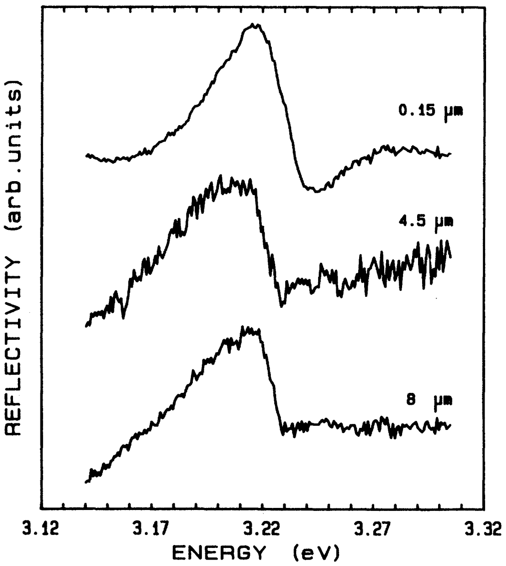

FIG. 2. Reflectivity spectra at 1.8 K of ZnSe epilayers grown on GaAs (100) for different thicknesses above the band-gap edge.

TABLE I. Reflection peak energies at 1.8 K of light-hole $E_{\rm lh}$, heavy-hole $E_{\rm hh}$, and $E_0+\Delta_0$ excitonic transitions, ratio of the shear deformation potential to the hydrostatic potential (b/a), and the value of the spin-orbit interaction Δ_0 of ZnSe layers grown on GaAs (100) as a function of the layer thickness.

Sample No.	e (μm)	$E_{\rm lh}$ (meV)	$E_{\rm hh}$ (meV)	$E_0+\Delta_0$ (meV)	Δ_0 (meV)	b/a
1	0.15	2814.7	2803.9	3235	425.7	0.217
2	1.5	2792.1	2798.2	3220.7	425.6	0.208
3	4.5	2793.3	2798.8	3221.5	425.5	0.221
4	6.5	2795.2	2799.4	3222.5	425.2	0.217
5	7	2795.2	2799.4	3222.7	425.4	0.230
6	8	2795.8	2799.4	3222.9	425.3	0.210
7	13	2795.8	2799.4	3222.9	425.3	0.210
8	14	2795.3	2798.8	3223	426	0.211

The value of the ratio of the shear and hydrostatic deformation potential denoted b/a is determined for each layer, using Eqs. (3) and (5) and taking the elastic stiffness constants given by Hodgins and Irwin[10]

$$\frac{b}{a}=\left[\frac{(C_{11}-C_{12})}{(C_{11}+2C_{12})}\right]\frac{\delta}{\Delta(E_0+\Delta_0)}\;. \tag{6}$$

B. Free excitons in ZnSe epilayers

Figure 1 presents the reflection spectra of ZnSe epilayers for different thicknesses measured at 1.8 K, in the spectral region of the ZnSe band edge. For a thin layer, with thickness around 0.15 μm, two exciton resonances, assigned to light-hole and heavy-hole excitonic transitions split by a compressive strain, are observed at a higher energy than the free-exciton transition of bulk ZnSe. This strain splitting decreases with increasing layer thickness, indicating the relaxation of the strain induced by the misfit dislocation introduced in the layer. Layers thicker than 1 μm suffer the opposite strain from that suffered by thin layers; this is displayed by the low-energy shift of the free-exciton resonances and the reverse of the light- and heavy-hole energies. Then the valence-band top is the heavy- (light-) hole band for thin (thick) epilayers.[15]

Figure 2 shows reflectance spectra in the spectral region above the band-gap edge of ZnSe. The resonance dip is associated with the excitonic transition from the Γ_7 (spin-orbit-split) valence band to the conduction band of ZnSe. Energy transition is taken at the inflection point. In spite of a broadened line characteristic of the $E_0+\Delta_0$ transition,[12,13,16] a redshift of this transition is observed with increasing layer thickness. Because of the known negative sign of the hydrostatic deformation potential ($a<0$), the shift of $E_0+\Delta_0$ indicates clearly the sign of the stress. For a layer thickness around 1 μm, the $E_0+\Delta_0$ excitonic transition is almost at the same energy as the $E_0+\Delta_0$ excitonic transition of bulk ZnSe, based on the lack of observed splitting of the transition at the band-gap edge.[17] For thinner (thicker) layer thickness, blueshift (redshift) of the energy transition indicates the compressive (tensile) stress in the layer.

Table I shows the reflectivity peak energies measured at 1.8 K for samples with different thicknesses and the ratio of deformation potentials (b/a), which is estimated using Eq. (6). We obtain the average value of this ratio $b/a=0.22\pm0.01$. Taking the value of the hydrostatic potential deformation $a=-5.4$ eV given by Ref. 18, we get $b=-1.19\pm0.05$ eV, in good agreement with the experimental data obtained by other methods.[8,18–20] The value of the spin-orbit interaction is also estimated for each layer [Eq. (4)] and seems not to be affected by the strain.[21] The average value $\Delta_0=(425.5\pm0.5)$ meV is in accordance with the experimental[16,19] and theoretical[22] bulk value.

The value of residual strain is then calculated by

TABLE II. Values of tne in-plane strain ϵ, of the stress σ, the experimental and calculated ratio of the heavy-hole-to-light-hole peak intensities, and the experimental ratio of the heavy-hole peak intensity to the heavy-hole peak intensity attributed to the first excited state ($n=2$) obtained by reflection measurements at 1.8 K on ZnSe layers grown on GaAs (100) as a function of the layer thickness.

Sample No.	e (μm)	ε (10^{-5})	σ (MPa)	$\left[\frac{I_{\rm hh}}{I_{\rm lh}}\right]_{\rm expt}$	$\left[\frac{I_{\rm hh}}{I_{\rm lh}}\right]_{\rm calc}$	$\left[\frac{I_{\rm 1hh}}{I_{\rm 2hh}}\right]_{\rm expt}$
1	0.15	−204	−158	2.8	2.85	
2	1.5	115	89	5.2	3.10	
3	4.5	104	80	5.2	3.08	10.6
4	6.5	79	61	4.3	3.06	10
8	14	66	51	7.4	3.05	12

$$\epsilon=\frac{C_{11}}{2b(C_{11}+2C_{12})}\delta \qquad (7)$$

and the stress is estimated by

$$\sigma=\frac{(C_{12}-C_{11})}{2b}\delta \ . \qquad (8)$$

In Fig. 3(a), the energies of light- and heavy-hole excitons are plotted as a function of strain given by Eq. (7). We note that the light-hole exciton energy is four times more sensitive to the stress variation than the heavy-hole exciton energy. The result of $E_0+\Delta_0$ dependence is displayed in Fig. 3(b). We observe a good agreement with the theoretical linear dependence of these excitonic transition energies with strain. For films thicker than 2 μm, reflectivity spectra reveal an additional signature at 13 meV higher energy than the heavy-hole ground-state free exciton. The ratio of intensities is in accordance with the oscillator strength of the excitonic transition (see Table II); these weak features, which are slightly sensitive to the strain, are attributed to the first excited ($n=2$) free exciton related to the heavy-hole band($J=\frac{3}{2}$, $m_J=\pm\frac{3}{2}$). The energy position of these lines is also in accordance with calculated linear dependence taking the free-exciton binding energy of 17 meV[23] for ZnSe at 1.8 K. In Fig. 4, a complete disappearance of the excited band is observed at a temperature of 45 K, which confirms the origin of this peak.

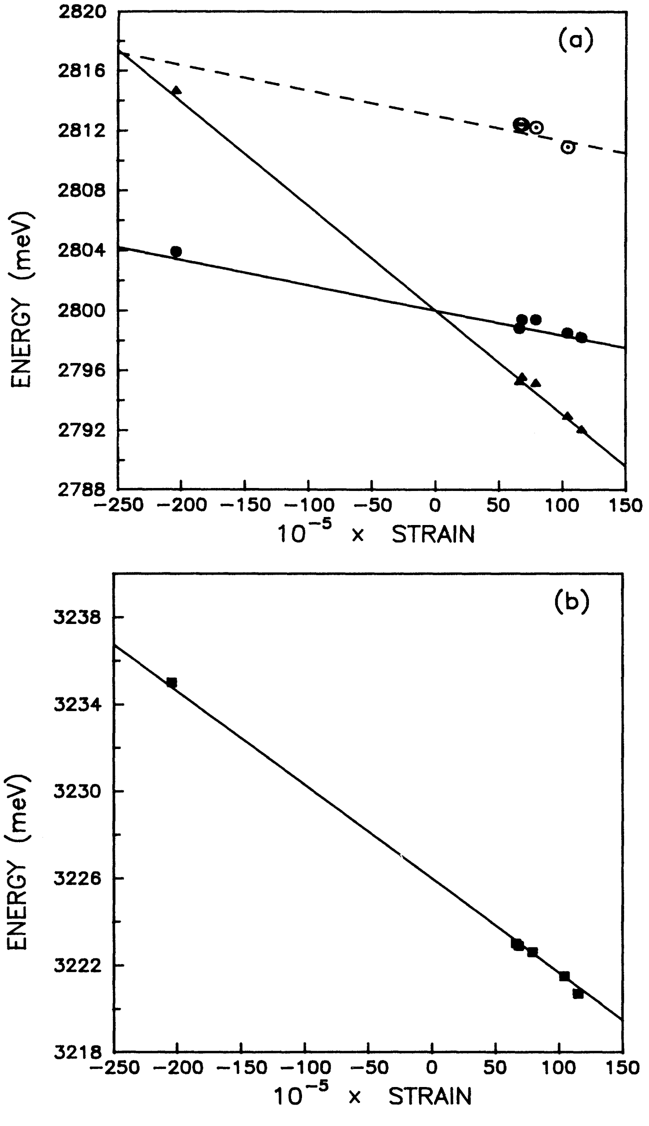

FIG. 3. (a) Energy shift of reflectivity structures at 1.8 K of ZnSe layers grown on GaAs (100) as a function of the in-plane strain. Experimental results are plotted by solid triangles (E_{lh}), solid circles (E_{hh}), and open circles (E_{hh}, $n=2$). The lines represent the calculated values of the excitons energies as a function of strain. (b) Dependence of the $E_0+\Delta_o$ transition energies with the in-plane strain determined at 1.8 K from reflection spectra of ZnSe layers grown on GaAs (100). Experimental data are plotted with solid squares. The solid line represents the calculated energy values as a function of the strain.

Figures 1 and 5 reveal the variation, with increasing layer thickness, in the ratio of light-hole exciton intensity to heavy-hole exciton intensity. Reflectivity spectra for samples under tensile stress indicate that the relative intensity of the light-hole excitonic transition is weaker than that for the sample under compressive stress. This fact is explained by the stress-inducing variation in intensity caused by the coupling between the light-hole valence band and the spin-orbit-split band.[12,13,19] The ratio of heavy-hole exciton intensity to light-hole exciton intensity is given by

$$\frac{I_{\mathrm{hh}}}{I_{\mathrm{lh}}}=3(1+2\alpha) \ , \qquad (9)$$

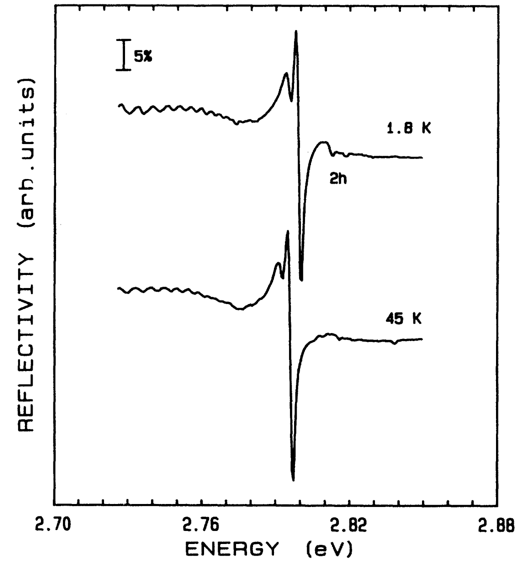

FIG. 4. Reflection spectra at 1.8 K and 45 K of a 14-μm ZnSe layer grown on GaAs (100) showing the influence of the temperature measurements on the feature associated with the first exicted free exciton ($n=2$) related to the heavy-hole band.

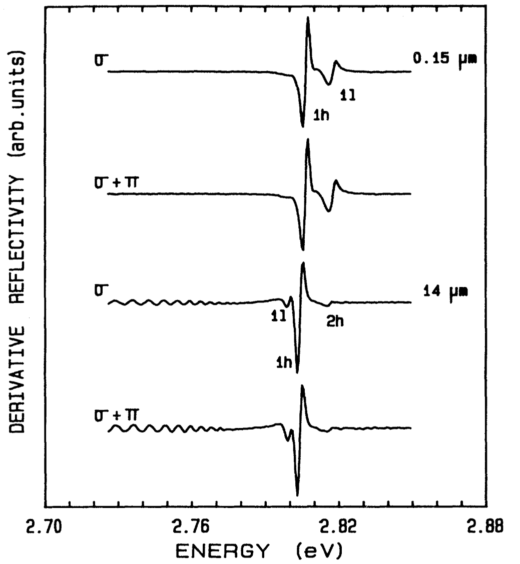

FIG. 5. Derivative reflection spectra with normal incidence at 1.8 K of ZnSe epilayers grown on GaAs (100) using polarized light for two different layer thicknesses (0.15 and 14 μm). Spectra labeled σ and $(\sigma+\pi)$ are taken with the electric vector direction indicated in Fig. 6.

with

$$\alpha=\frac{2|b|(C_{11}+2C_{12})}{C_{11}}\frac{\epsilon}{\Delta_0} .$$

In Table II, the values of the intensity ratio $I_{\mathrm{hh}}/I_{\mathrm{lh}}$ as calculated from Eq. (9) are compared with the experimental values taken from Fig. 1. The theoretical values are in qualitative agreement with experiment. However, we note that for layers thinner than 1 μm, the oscillator structure due to interference effects may disturb the relative intensities of excitonic transitions.

Figure 5 presents the derivative reflectivity spectra of two samples in the normal incidence light, with different polarizations (see Fig. 6). For the same samples, we observe a change of the intensity of the light-hole exciton in two linear polarizations. This may be attributed to the misorientation of the epilayer, probably induced by the substrate misorientation.[7] Our x-ray-diffraction measurement similar to that given in Ref. 7 has confirmed this fact. Then, the enhancement of light-hole exciton intensity in $(\sigma+\pi)$ polarization (Fig. 6) is expected by the relation

$$\frac{I_{\mathrm{lh}}^{(\sigma+\pi)}-I_{\mathrm{lh}}^{\sigma}}{I_{\mathrm{lh}}^{\sigma}}\simeq 2\Delta\theta^2\,(2+\alpha) , \tag{10}$$

where $I_{\mathrm{lh}}^{(\sigma+\pi)}$, I_{lh}^{σ} are light-hole intensities observed with the electric-field direction parallel and normal to the [010] direction, respectively and $\Delta\theta$ is the disorientation angle.

Equation (10) indicates that the enhancement of light-hole intensities in $(\sigma+\pi)$ polarization is higher in the case of tensile stress than in the case of compressive stress. This is in accordance with the experimental results shown in Fig. 5.

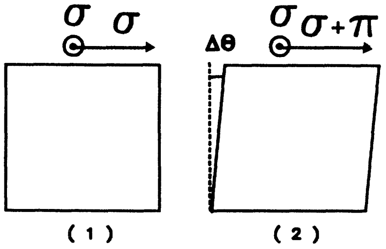

FIG. 6. Schematic representation of the polarization effect in the reflection experiment with normal incidence. (1) is for a layer without misorientation; (2) is for a layer grown with a disorientation angle $\Delta\theta$.

The variation of strain with increasing thickness shown in Fig. 7 indicates the relaxation of both thermal strain and strain due to the lattice mismatch. The thermal strain decreases for epilayers thicker than 4 μm. For thicker layers, the amount of thermal strain is less than the thermal strain (ϵ_{the}) calculated for samples cooled from the growth temperature (800 K) to the measurement temperature (1.8 K), assuming no relaxation (see Ref. 8). This may be attributed to a compressive stress occurring at growth temperature in the epilayers.[24] Moreover, thicker layers may distort the substrate at the interface and the mismatch will also be compensated for by a two-dimensional tension of the GaAs substrate. It is noted

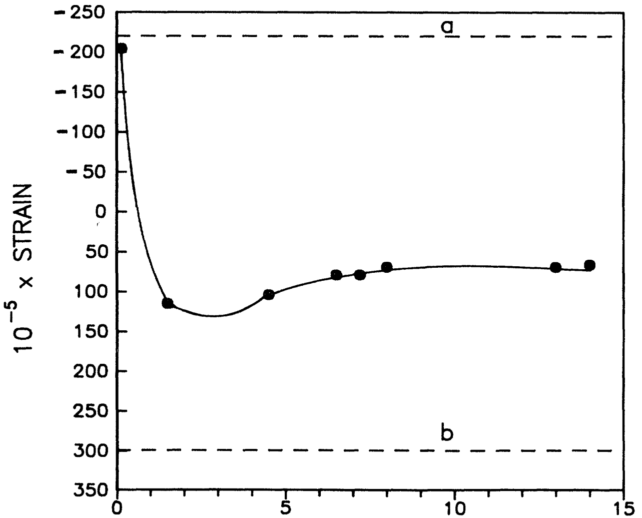

FIG. 7. In-plane strain in ZnSe epilayers grown on GaAs (100) as a function of the layers thickness from reflection data at 1.8 K. The dashed line (a) corresponds to the calculated strain induced by the lattice mismatch at the measurement temperature and (b) corresponds to the calculated strain taking into account the growth and the measurement temperatures (assuming no relaxation in both caes). The solid line is added for clarity.

that modulation reflectivity spectroscopies[2] for the spectral range in the vicinity of the GaAs band edge have revealed a two-dimensional tensile stress of the GaAs substrate of thick ZnSe epilayers.

IV. CONCLUSION

ZnSe epilayers grown as GaAs have allowed us to study the variation of strain with increasing thicknesses. From the observation of the effect of strain on the $E_0+\Delta_0$ excitonic transition, we are able to estimate the value of the ratio of deformation potentials (b/a), which is in good accordance with previous results. The positions of excitonic transition energies and their oscillator strengths are investigated. Polarization effects reveal the disorientation of the layer.

ACKNOWLEDGMENTS

Groupe d'Etude des Semiconducteurs is "Unité No. 357 du Centre National de la Recherche Scientifique" and Laboratoire de Physicochimie des Matériaux Solides is "Unité Associée No. 407 du Centre National de la Recherche Scientifique".

---

[*] On leave from Unité de Développement des Techniques du Silicium, Haut Commissariat à la Recherche Algiers, Algeria.

[1] T. Yao, Y. Okada, S. Matsui, K. Ishida, and I. Fujimoto, J. Cryst. Growth **81**, 518 (1987).

[2] Y. R. Lee, A. K. Ramdas, L. A. Kolodziejski, and R. L. Gunshor, Phys. Rev. B **38**, 13 143 (1988).

[3] K. Ohkawa, T. Mitsuyu, and O. Yamazaki, Phys. Rev. B **38**, 12 465 (1988).

[4] K. Shahzad, Phys. Rev. B **38**, 8309 (1988).

[5] G. Kuldeck, N. Presser, J. Gutowski, K. Hingerl, H. Sitter, S. M. Durbin, D. R. Meuke, M. Kobayashi, and R. L. Gunshor, J. Appl. Phys. **68**, 5630 (1990).

[6] R. L. Aulombard, M. Averous, O. Briot, J. Calas, D. Coquillat, F. Hamdani, J. P. Lascaray, N. Moulin, and N. Tempier, J. Cyrst. Growth **101**, 204 (1990).

[7] A. Ohki, N. Shibata, and S. Zembutsu, J. Appl. Phys. **64**, 694 (1988).

[8] J. Gutowski, N. Presser, and G. Kudleck, Phys. Status Solidi A **120**, 11 (1990).

[9] J. Petruzzelo, B. L. Greenberg, D. A. Cammack, and R. Dalby, J. Appl. Phys. **63**, 2299 (1988).

[10] C. G. Hodgins and J. C. Irwin, Phy. Status Solidi A **28**, 647 (1975).

[11] This approximation is available in the case of II-VI compounds (see Refs. 12, 13, and 19).

[12] M. Chandrasekhar and F. H. Pollack, Phys. Rev. B **15**, 2127 (1977); F. H. Pollack, Surf. Sci. **37**, 863 (1973).

[13] F. H. Pollack and M. Cardona, Phys. Rev. **172**, 816 (1968).

[14] We assume that the three valence bands have the same exciton binding energy, which is not affected by the stress (see Refs. 12 and 13).

[15] Thin and thick layers refer to layers thinner or thicker than 1 μm, respectively.

[16] B. Segall and D. T. F. Marple, in *Physics and Chemistry of II–VI Compounds,* edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), p. 319.

[17] D. Coquillat, F. Hamdani, J. P. Lascaray, O. Briot, N. Briot, and R. L. Aulombard (unpublished).

[18] A. Blacha, H. Presting, and M. Cardona, Phys. Status Solidi B **126**, 11 (1984).

[19] D. W. Langer, R. N. Euwema, K. Era, and T. Koda, Phys. Rev. B **2**, 4005 (1970).

[20] R. L. Gunshor, L. A. Kolodziejski, M. R. Melloch, M. Vaziri, C. Choi, and N. Otsura, Appl. Phys. Lett. **50**, 200 (1987); A. Pesek, K. Hingerl, K. Lischka, E. Fautner, T. Ryan, G. Kudlek, J. Gutowski, and B. Muller, in *Proceedings of the 20th International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 981.

[21] P. J. Melz and I. B. Ortenburger, Phys. Rev. **3**, 3257 (1971).

[22] P. Eckelt, Solid. State Commun. **6**, 484 (1968).

[23] H. Venghaus, Phys. Rev. B **19**, 3071 (1979).

[24] G. Landa, R. Carles, C. Fontaine, E. Bedel, and A. Muroz-Yague, J. Appl. Phys. **66**, 196 (1989).