

Strain-induced splitting of the heavy-hole- and light-hole-exciton energies in NaI thin films

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Optical absorption spectra and x-ray-diffraction patterns of NaI thin films grown by vacuum evaporation onto alkali-halide substrates (NaCl, KCl, RbCl, and KBr) have been studied. The (Γ_8^-, Γ_6^+) -exciton energy in the films depends strongly on the materials of substrates and on the values of lattice mismatches between the NaI films and substrates. The NaI films in NaI/KBr and NaI/RbCl with small positive lattice mismatches (+1.9% and +1.7%) show splittings of the exciton-absorption peak, which are caused by the biaxial strains arising from the heteroepitaxial growth: The strains remove the degeneracy of the heavy-hole and light-hole energies at the Γ_8^- state. The critical thicknesses of the NaI films, at which the strains begin to relax, are estimated to be 50 Å for NaI/KCl and 100 Å for NaI/KBr and NaI/RbCl. We discuss these results in terms of the concept of the epitaxial growth of the films. [S0163-1829(98)10503-9]

I. INTRODUCTION

Thin films of alkali halides evaporated onto LiF or quartz substrates have been widely used for measurements of optical spectra in the fundamental absorption region.¹⁻⁶ The spectra are often regarded as a standard, although the spectra are more or less affected by the strains in the films. Recently, Nishimura *et al.*⁷ have studied the optical properties of RbI films evaporated onto several alkali-halide and amorphous-quartz substrates and found that the absorption and luminescence spectra of the films depend strongly on the substrates. They discussed that the films had two kinds of biaxial strains: (i) lattice-mismatch strains due to the heteroepitaxial growth and (ii) thermal strains between the films and substrates. The RbI film in RbI/RbBr with the smallest lattice mismatch (-6.2%) in these systems showed the largest lattice-mismatch strain and smallest thermal strain, while the film in RbI/LiF with the largest lattice mismatch (-45%) showed the smallest lattice-mismatch strain and largest thermal strain, from which they concluded that the lattice-mismatch strain relaxed partially in RbI/RbBr and perfectly in RbI/LiF.

The energy shift of the exciton-absorption peak has also been observed by Ejiri and Nakagawa^{8,9} for multilayered alkali-halide systems (e.g., KCl-KBr) and by Edamatsu, Hirota, and Hirai¹⁰ for similar systems (e.g., KI-KBr). Ejiri and Nakagawa assumed a quantum confinement for the energy shift, while Edamatsu, Hirota, and Hirai assumed a mixed crystallization. Since the lattice mismatches in these systems were not very large, 4.8% for KCl-KBr and 6.6% for KI-KBr, these authors had to pay attention to the lattice-mismatch strains as well as to the quantum confinement and mixed crystallization.

In the present study, we investigate NaI thin films evaporated onto alkali-halide substrates. In NaI/RbCl and NaI/KBr with small lattice mismatches (+1.7% and +1.9%, respectively), the NaI films of 50 Å in thickness keep the strains due to the lattice mismatches unrelaxed, so that the films show large shifts and splittings of the (Γ_8^-, Γ_6^+) -exciton peak. We discuss these results in terms of the concept of the lattice-mismatch strain arising from the heteroepitaxial growth of the films.

II. EXPERIMENT

NaI thin films with various thicknesses were made with a growth rate of 1 Å/s by evaporation in a vacuum chamber with a pressure 2×10^{-4} Pa onto alkali-halide substrates (NaCl, KCl, RbCl, and KBr) at room temperature. The film thicknesses were determined by a quartz oscillator, which made it possible to determine the deposition rate and the total deposition thickness at any time during the growth of films. The quartz oscillator was calibrated by a profilometer. The surfaces of the highly hygroscopic NaI films were covered with less hygroscopic materials such as NaCl, KCl, RbCl, and KBr. The x-ray-diffraction patterns of the films were observed by the Cu $K\alpha$ line of a diffractometer. We cut the $K\beta$ line with a Ni filter. Optical absorption and reflection spectra were measured by a spectrophotometer and by a reflectometer, respectively. The spectral resolutions of these systems were both 2 Å.

III. RESULTS

Figure 1 shows the θ - 2θ x-ray-diffraction patterns measured at room temperature for three samples: NaI/KBr, NaI/NaCl, and NaI/KCl. The NaI films in the samples are all 500 Å thick and covered with NaCl, 2500 Å thick. All the patterns show the (200) and (400) lines of the NaI films and those of the substrates. The patterns also show the (200) lines of the NaCl cap layers. These x-ray patterns indicate that the NaI films and the NaCl cap layers grow along the [001] direction normal to the substrates. The accuracy and resolution of the diffractometer were not sufficient to evaluate the quality and strain of the films.

Figure 2 shows the absorption spectra measured at 50 K for four samples: NaI/KCl, NaI/NaCl, NaI/KBr, and NaI/RbCl. The NaI films are all 50 Å thick and covered with the same materials, 1000 Å thick, as the substrates. These spectra are not corrected for the reflection loss. The broken line depicted at 5.600 eV represents the $1s$ - (Γ_8^-, Γ_6^+) -exciton energy (E_{1s}) in bulk NaI at 50 K, which was estimated from the luminescence and reflection spectra due to free excitons. The spectra show that the exciton energy depends strongly on the materials of substrates and on the values of lattice mismatches (Table I).

The exciton energy in NaI/KCl is larger by 110 meV than E_{1s} , while the energies in NaI/KBr and NaI/RbCl are smaller by 80 and 84 meV, respectively, than E_{1s} . These

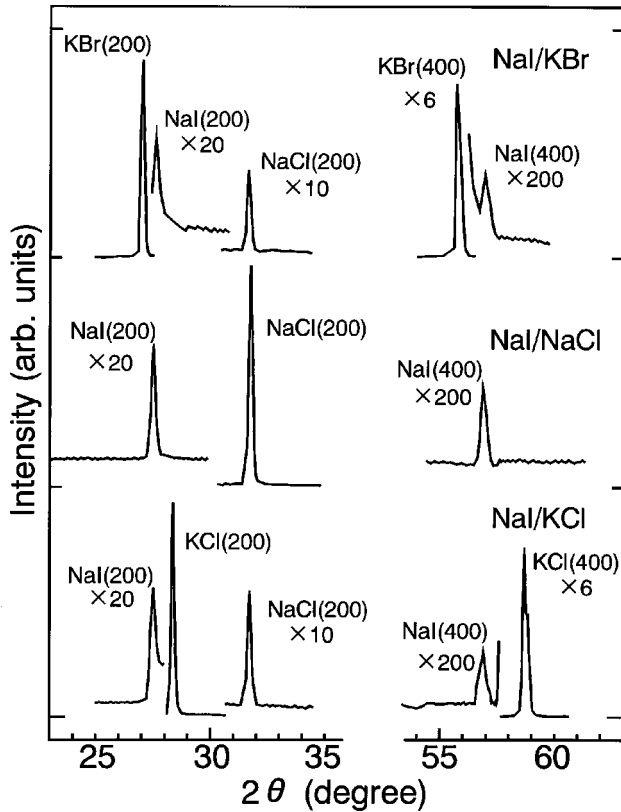


FIG. 1. X-ray-diffraction patterns measured at room temperature for the NaI/KBr, NaI/NaCl, and NaI/KCl samples. The NaI films are all 500 Å thick and covered with NaCl of 2500 Å in thickness.

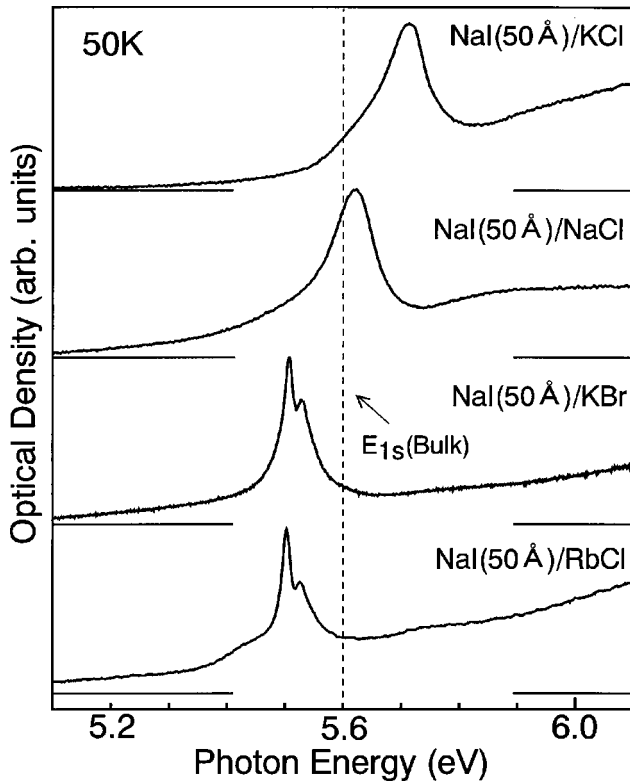


FIG. 2. Absorption spectra measured at 50 K for the NaI/KCl, NaI/NaCl, NaI/KBr, and NaI/RbCl samples. The NaI films are all 50 Å thick. The spectral resolution was 2 Å. The broken line depicted at 5.600 eV shows the 1s-exciton energy (E_{1s}) in bulk NaI at 50 K.

TABLE I. Values of the lattice constants a_0 of alkali halides used as the substrates and those of the lattice mismatches between NaI and the substrates. The lattice mismatch f is defined by $[\{a_0(\text{substrate}) - a_0(\text{NaI})\}/a_0(\text{NaI})] \times 100$, where the lattice constant of NaI is 6.474 Å.

Alkali halide	a_0 (Å)	f (%)
NaCl	5.640	-13
KCl	6.239	-2.8
RbCl	6.582	+1.7
KBr	6.598	+1.9

energy shifts must be caused by the lattice-mismatch strains arising from the heteroepitaxial growth of the NaI films on the respective substrates: The strain in NaI/KCl with a negative lattice mismatch (-2.8%) is compressive and the strains in NaI/KBr and NaI/RbCl with positive lattice mismatches (+1.9% and +1.7%) are tensile. Here we confirmed the fact that the exciton energy in bulk NaI shifted to higher energy under hydrostatic pressure.¹¹

The absorption spectra of NaI/KBr and NaI/RbCl suffering tensile strains show splittings of the 1s-exciton peak, while that of NaI/KCl suffering compressive strain does not show such a splitting. The spectrum of NaI/NaCl with a large lattice mismatch (-13%) does not show splitting or a remarkable energy shift, suggesting a strong relaxation of the lattice-mismatch strain.

Figure 3 shows a comparison of the reflection and absorption spectra measured at 7 K for NaI/RbCl. The NaI film is 50 Å thick and covered with RbCl, 1000 Å thick. A sharp doublet structure of the 1s-exciton peak is observed in the reflection spectrum as well as in the absorption spectrum. The 1s-exciton peak is accompanied by two humps. Although the hump denoted by 2s can be assigned to the 2s-exciton peak, the origin of the hump located at the low-energy side of the 1s-exciton peak is not known at present.

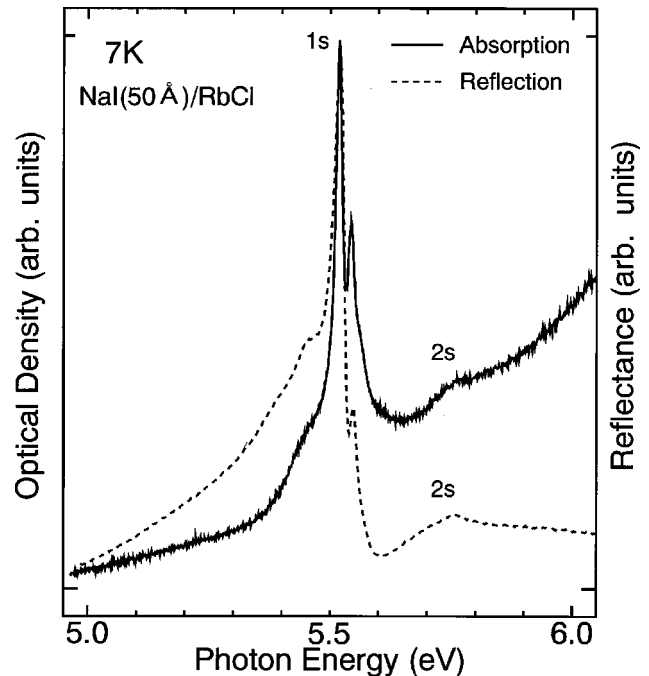


FIG. 3. Reflection and absorption spectra measured at 7 K for the NaI/RbCl samples. The spectral resolutions for these spectra were both 2 Å.

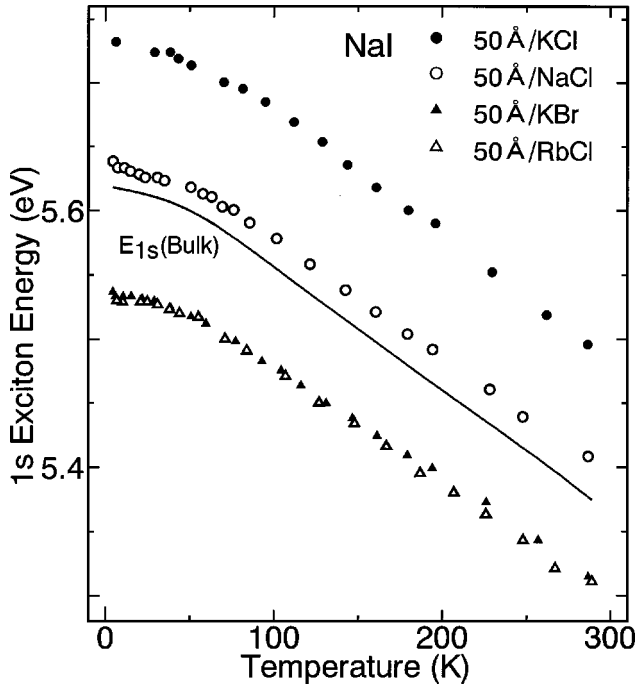


FIG. 4. The $1s$ -exciton energies for the NaI/KCl, NaI/NaCl, NaI/KBr, and NaI/RbCl samples as a function of temperature. The NaI films are all 50 Å thick. The solid curve shows the temperature dependence of the $1s$ -exciton energy (E_{1s}) in bulk NaI.

The $1s$ -exciton energies in NaI/KCl, NaI/NaCl, NaI/KBr, and NaI/RbCl are shown in Fig. 4 as a function of temperature. The NaI films are all 50 Å thick and covered with the same materials, 1000 Å thick, as the substrates. The exciton energies in NaI/KBr and NaI/RbCl are nearly equal to each

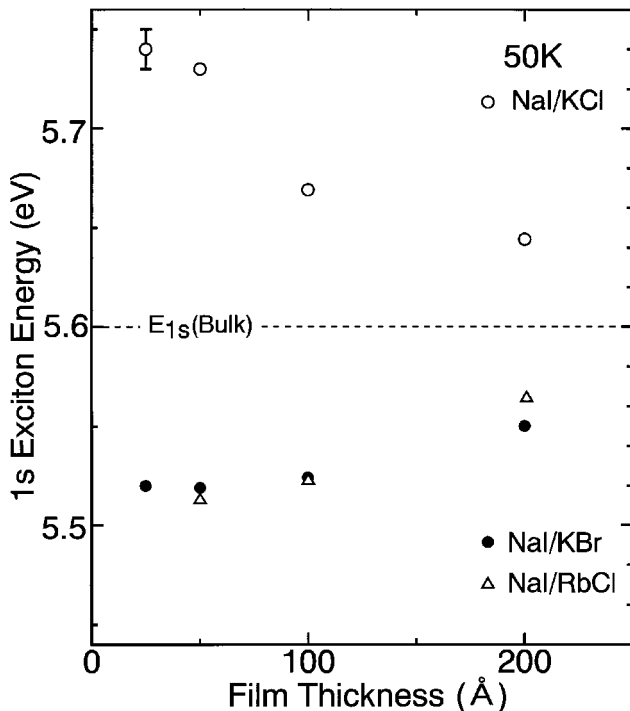


FIG. 5. The $1s$ -exciton energies for the NaI/KCl, NaI/KBr, and NaI/RbCl samples as a function of NaI film thickness. The broken line depicted at 5.600 eV shows the $1s$ -exciton energy (E_{1s}) in bulk NaI at 50 K.

other throughout the whole temperature range measured and are completely different from the energies in NaI/KCl and NaI/NaCl. The exciton energies in these four samples change in the same way as that of bulk NaI (solid curve) obtained from the luminescence and reflection spectra due to free excitons, which suggests that the strains arising from the heteroepitaxial growths are kept over the wide temperature range.

In Fig. 5 the $1s$ -exciton energies in NaI/KCl, NaI/KBr, and NaI/RbCl are shown as a function of NaI-film thickness. The NaI films are covered with the same materials, 1000 Å thick, as the substrates. The energy in NaI/KCl is nearly constant below 50 Å and approaches E_{1s} above 50 Å, while the energies in NaI/KBr and NaI/RbCl are almost constant below 100 Å and approach E_{1s} above 100 Å. These results suggest that the thicknesses, 50 Å in NaI/KCl and 100 Å in NaI/KBr and NaI/RbCl, correspond to the critical thicknesses, at which the lattice-mismatch strains begin to relax, in the respective films. It is noted that the critical thicknesses are comparable to those in $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ and $\text{Si}_x\text{Ge}_{1-x}/\text{Si}$ strained heterojunctions.¹²

IV. DISCUSSION

Epitaxial growths of evaporated thin films of alkali halides have been studied by Schulz¹³ by means of reflection high-energy-electron diffraction. Yang and Flynn^{14,15} and Saiki, Nakamura, and Koma¹⁶ recently have applied the molecular-beam epitaxy (MBE) to the epitaxial growth of alkali-halide films. The latter group reported that in KCl/KBr with a small lattice mismatch (+4.8%), two-dimensional layer-by-layer growth of KCl film occurred from the initial stage of MBE deposition and even a very thin film (7 Å) covered the KBr substrate uniformly. Similarly, Nishimura *et al.*⁷ reported that RbI films had large strains arising from the epitaxial growths. Taking these results into account, we discuss the shifts and splittings of the $1s$ -exciton energies for the NaI films, shown in Figs. 2–5.

In the absence of strain, the spin-orbit interaction splits the p -like valence-band state in NaI into fourfold degenerate Γ_8^- state and twofold degenerate Γ_6^- state. The energy difference between the Γ_8^- and Γ_6^- states is known to be very large in NaI (1.15 eV).⁶ From the well-known optical properties of strained heterojunctions in semiconductors,¹⁷ we expect that the biaxial strain in NaI films due to lattice mismatches removes the degeneracy of the Γ_8^- state: heavy-hole and light-hole states. Since the strain-induced splittings in NaI films (Figs. 2 and 3) are much smaller than the spin-orbit splitting (1.15 eV), the strain-induced shifts of the heavy-hole and light-hole energies ΔE_{hh} and ΔE_{lh} are approximately given by¹⁸

$$\Delta E_{hh} = -\Delta E_H - \Delta E_S/2 \quad (1a)$$

and

$$\Delta E_{lh} = -\Delta E_H + \Delta E_S/2, \quad (1b)$$

where ΔE_H and ΔE_S , which are the hydrostatic and shear terms, are given by

$$\Delta E_H = 2a\{(C_{11} - C_{12})/C_{11}\}\varepsilon_{\parallel} \quad (2a)$$

and

$$\Delta E_S = -2b\{(C_{11} + 2C_{12})/C_{11}\}\varepsilon_{\parallel}. \quad (2b)$$

Here a and b represent the respective deformation potentials,

C_{11} and C_{12} are the elastic stiffness constants, and ε_{\parallel} is the in-plane biaxial strain. We define $\varepsilon_{\parallel} > 0$ for a tensile strain and $\varepsilon_{\parallel} < 0$ for a compressive strain.

The s -like conduction-band (Γ_6^+) state, on the other hand, does not split under the strain, but shifts due to the hydrostatic term of the strain:

$$\Delta E_c = 2c\{(C_{11} - C_{12})/C_{11}\}\varepsilon_{\parallel}, \quad (3)$$

where c is the deformation potential. Assuming that the strain effect on the exciton binding energy is negligible, the energy shifts of the heavy-hole and light-hole excitons ΔE_{HH} and ΔE_{LH} are approximately given by

$$\Delta E_{\text{HH}} = \Delta E_c - \Delta E_{\text{hh}} = \Delta E'_H + \Delta E_S/2 \quad (4a)$$

and

$$\Delta E_{\text{LH}} = \Delta E_c - \Delta E_{\text{lh}} = \Delta E'_H - \Delta E_S/2, \quad (4b)$$

where $\Delta E'_H = 2(a+c)\{(C_{11} - C_{12})/C_{11}\}\varepsilon_{\parallel}$.

We first discuss the energy shifts of the $1s$ -exciton peaks shown in Fig. 2. As described above, the high-energy shift in NaI/KCl occurs from the hydrostatic term of the compressive strain and the low-energy shifts in NaI/KBr and NaI/RbCl occur from the same term of the tensile strains. Since the thickness (50 Å) of the NaI films is smaller than the respective critical thicknesses (50 Å in NaI/KCl and 100 Å in NaI/KBr and NaI/RbCl) estimated from the thickness dependence of the $1s$ -exciton energies (Fig. 5), we assume that the in-plane strains ε_{\parallel} coincide with the values of the lattice mismatches.

Based on above considerations, we estimate the value of deformation potential $a+c$ in the NaI films from $\Delta E'_H$ to be -2.8 eV for NaI/KCl, -3.0 eV for NaI/KBr, and -3.5 eV for NaI/RbCl. Among these values, -3.5 eV in NaI/RbCl with the smallest lattice mismatch ($+1.7\%$) is most reliable because the small lattice mismatch is favorable for homogeneous strain with less dislocation. The tensile strain in NaI/RbCl is also favorable for homogeneous strain because the curve of cohesive energy in a crystal lattice is generally asymmetric and is flat for lattice expansion rather than for lattice compression. This deduction is supported by the spectrum of NaI/KCl with a compressive strain (-2.8%), which shows a broad peak and no splitting of the $1s$ -exciton energy. For NaI/NaCl with a large negative lattice mismatch

TABLE II. Values of deformation potentials $a+c$ and b obtained from the exciton transitions in the NaI films.

Systems	$a+c$ (eV)	b (eV)
NaI/KCl	-2.8	
NaI/KBr	-3.0	$+0.18$
NaI/RbCl	-3.5	$+0.22$

(-13%), a small energy shift and broad width are observed, which suggests that the lattice-mismatch strain relaxes strongly in the film.

Next we discuss the splittings of the $1s$ -exciton peaks in NaI/KBr and NaI/RbCl shown in Fig. 2. Considering that the splittings occur from the shear term (ΔE_S) of the tensile strains, we estimate the value of the deformation potential b from ΔE_S to be $+0.18$ eV for NaI/KBr and $+0.22$ eV for NaI/RbCl. Since the oscillator strength of the exciton transition at the Γ point is considered to be three times stronger for the heavy-hole exciton than for the light-hole exciton in the light propagation along the $[100]$ axis from the basis functions¹⁹ and the spectra show that the low-energy peak in the doublet structure is much stronger than the high-energy peak, we conclude that the heavy-hole-exciton state lies at the lower-energy side than the light-hole-exciton state. To satisfy this condition, we must choose a positive value for b in Eqs. 4(a) and 4(b). These values of $a+c$ and b that we obtained are given in Table II. As far as we know, this is the first report for the values of deformation potentials in NaI.

Finally, we discuss the features of the reflection spectrum shown in Fig. 3. The reflection peak is very sharp (~ 20 meV in a full width at half maximum) and coincides in energy with the absorption peak. These features are quite different from those of bulk NaI crystal, in which the reflection peak shows a broad width corresponding to the energy difference between the transverse and longitudinal excitons (70 meV in NaI) and the peak is located at the high-energy side of the absorption peak. The reflection spectrum of the NaI film thus suggests that the reflection in a very thin film occurs strongly for the incident light whose energy corresponds to the transverse-exciton energy (E_{1s}). This is due to the fact that the light under this condition is extremely evanescent inside a crystal.

¹R. Hilsch and R. W. Pohl, Z. Phys. **59**, 812 (1930).

²P. L. Hartman, J. R. Nelson, and J. G. Siegfried, Phys. Rev. **105**, 123 (1957).

³W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).

⁴J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

⁵F. Fischer, Z. Phys. **160**, 194 (1960).

⁶K. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).

⁷H. Nishimura, T. Ohashi, S. Kawase, and M. Nakayama, J. Phys. Soc. Jpn. **64**, 3514 (1995).

⁸A. Ejiri and K. Nakagawa, J. Phys. Soc. Jpn. Lett. **58**, 2669 (1989).

⁹A. Ejiri and K. Nakagawa, Solid State Commun. **73**, 849 (1990).

¹⁰K. Edamatsu, S. Hirota, and M. Hirai, J. Phys. Soc. Jpn. **61**, 2543 (1992).

¹¹H. Nishimura, K. Kitano, S. Kawase, and M. Nakayama (unpublished).

¹²I. J. Fritz, Appl. Phys. Lett. **51**, 1080 (1987).

¹³L. G. Schulz, Acta Crystallogr. **5**, 130 (1952).

¹⁴M. H. Yang and C. P. Flynn, Phys. Rev. Lett. **62**, 2476 (1989).

¹⁵M. H. Yang and C. P. Flynn, Phys. Rev. B **41**, 8500 (1990).

¹⁶K. Saiki, Y. Nakamura, and A. Koma, Surf. Sci. **250**, 27 (1991).

¹⁷For a review see J. Y. Marzin, *Heterojunctions and Semiconductor Superlattices*, edited by G. Allan and G. Bastard (Springer-Verlag, Berlin, 1986), p. 161.

¹⁸M. Chandrasekhar and F. H. Pollak, Phys. Rev. B **15**, 2127 (1977).

¹⁹Y. Onodera and M. Okazaki, J. Phys. Soc. Jpn. **21**, 2400 (1966).