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Electronic structure of an InAs monomolecular plane in GaAs

Kenji Shiraishi and Eiichi Yamaguchi
Basic Research Laboratories, Nippon Telegraph and Telephone Corporation, 3-9-11 Midori-cho, Musashino-shi, Tokyo 180, Japan

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The electronic structure of an InAs monomolecular plane in the host GaAs is calculated by a self-consistent pseudopotential method. In this monomolecular-plane–host-crystal system, both electrons and holes are found to be strongly localized near the inserted InAs plane. The inserted InAs plane behaves somewhat like a quantum well. This result successfully explains the observed intense photoluminescence spectra. We also calculate the band structure for a system of two InAs monomolecular planes separated by N monolayers of GaAs. The calculated band gap as a function of GaAs thickness between the two InAs planes is in good agreement with experimental data.

I. INTRODUCTION

A monomolecular-plane–host-crystal system is a fascinating superlattice structure. In this system, a monolayer plane of a particular material is inserted into a different host material.[1] In this paper, we denote the system with a monomolecular plane of material B inserted into host material A as the $B(A)$ monomolecular-plane–host-crystal system (see Fig. 1), or simply as a monomolecular-plane system.

With ordinary superlattices, to synthesize stable superlattices we must select lattice-matched materials as constituents. However, by introducing a monomolecular plane, lattice-mismatched materials can also be synthesized. This is because in a monomolecular-plane–host-crystal system the excess energy of mismatched strain is confined to within the inserted-monomolecular-plane region. Thus these systems will extend the range of candidate constituent materials for use in superlattice physics, yielding various combinations of band gaps and band discontinuities. This result expands the field of band-gap engineering and artificial control of electron-hole spatial distribution. New types of properties and devices are expected to result from the synthesis of monomolecular-plane–host-crystal systems.

Using ordinary crystal-growth techniques, such as molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), it is still difficult to synthesize ideal interfaces because diffusion near the interface region cannot be ignored. This is because ordinary crystal-growth techniques require rather high crystal-growth temperatures. However, remarkable recent progress in crystal-growth technique has led to new epitaxial techniques such as flow-rate modulation epitaxy (FME)[2] and migration-enhanced epitaxy (MEE).[3] These methods can grow layer structures of III-V compounds at relatively low temperatures. In FME, a modified MOCVD method, organometals and arsines are fed alternately into a reaction chamber. The growing surface is kept flat during the FME growth as a result of the enhanced migration of metal atoms.

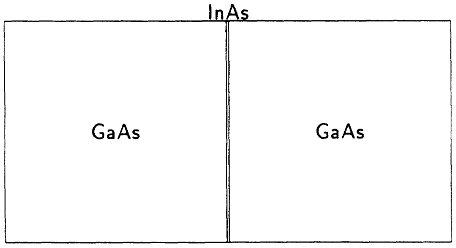

FIG. 1. Structure of monomolecular-plane–host-crystal system.

Using the FME method, Sato *et al.* have succeeded in synthesizing the ideal InAs(GaAs) monomolecular-plane system.[1] They observed low-temperature (2-K) photoluminescence with high intensity, small line width and polarization parallel to the interface. They studied the optical properties of a system consisting of two InAs planes separated by N-monolayer planes of GaAs, and also observed intense, narrow photoluminescence.

In this paper we consider monomolecular-plane systems and try to clarify the interesting features of their electronic properties by calculating the band structure from first principles. In particular, we investigate the InAs(GaAs) monomolecular-plane system which Sato *et al.* have succeeded in synthesizing. The self-consistent psuedopotential method based on the Hohenberg-Kohn-Sham local-density-functional formalism is employed to calculate the monomolecular-plane system.

The organization of this paper is as follows. In Sec. II the method of calculation is described. In Sec. III the numerical results of the electronic structure of InAs(GaAs) monomolecular-plane system are presented, and in Sec. IV the main results are summarized and discussed.

II. METHOD OF CALCULATION

In the present study, we use the $(\mathrm{InAs})_1/(\mathrm{GaAs})_n$ superlattice model to describe the InAs(GaAs) monomolecular-plane system (see Fig. 2). In this calcula-

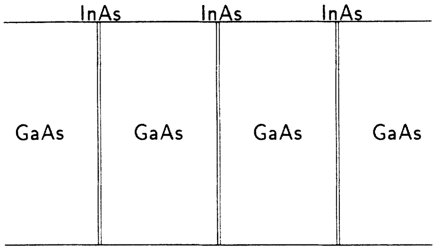

FIG. 2. Structure of $(InAs)_1/(GaAs)_n$ superlattice model.

tion, first we determine the position of each atom by minimizing the total energy, and then investigate the electronic structure. To calculate the total energy, we use an *ab initio* pseudopotential method[4] within the Hohenberg-Kohn-Sham local-density-functional (LDF) formalism.[5] On the other hand, to obtain the energy gap, we use the semiempirical pseudopotential method introduced by Nakayama *et al.*[6,7]

A. Total-energy calculations

To calculate the total energy, we use the *ab initio* pseudopotential method. This method has been demonstrated to give accurate results in describing a variety of structural properties of many kinds of materials.[8] The valence electron plays a dominant role determining the structural properties of the system; therefore, the effect of core state can reasonably be neglected. Thus, the pseudopotential approach, which neglects the core state, gives good results for structural properties.

The ionic pseudopotentials used in the present study are nonlocal ones. The validity of this potential is checked by calculating the bulk properties. The calculated and measured bond lengths of bulk GaAs and bulk InAs are compared in Table I. The valence wave functions are described using a plane-wave basis set. The exchange-correlation interactions are approximated by an $X\alpha$ potential with exchange $\alpha = 0.7$.[10] For the cutoff parameter, plane waves up to 11.9 Ry in kinetic energy are included in the basis set.

B. Energy-gap calculations

Within the LDF formalism, calculated band-gap energies for semiconductors and insulators are always smaller than the experimentally measured ones, often by 50% or more. This is because LDF does not include an accurate self-energy potential in the equation of calculating excitation spectra. Thus, in order to clarify the electronic structures of the excited state, we adopt the semiempirical pseudopotential method introduced by Nakayama *et al.*[6,7] In their treatment, the exchange-correlation potential is approximated by the $X\alpha$ method with $\alpha = 1.15$ to fit the experimental band gaps. This large value of α corresponds to the fact that a large exchange-correlation potential is effective in a region where a valence charge exists and as a result the energy gain of a valence-band state due to the attractive potential becomes large. On the other hand, conduction-band states are less influenced by the local change of exchange-correlation potential. Therefore band-gap energies are shifted by nearly a constant. This semiempirical treatment can be compared to the recent quasiparticle treatment. Hybertsen and Louie[11] calculated the quasiparticle energy of semiconductors and insulators in Hedin's *GW* formalism, which are in good agreement with experimentally determined levels. According to their analysis on the self-energy potential, due to the local-field effect (nonlocal screening and Coulomb-hole effects) of the self-energy correction, the electrons in a bond region feel stronger screening and Coulomb-hole effects than those obtained in the LDF formalism, while the electrons in an interstitial region feel weaker screening and Coulomb-hole effects. The semiempirical treatment in the present work is considered to reflect the above feature of self-energy correction.

TABLE I. Comparison of the calculated and measured bond lengths.

	GaAs	InAs
Calculation	2.39 Å	2.56 Å
Experiment	2.45 Å[a]	2.62 Å[a]

[a] Reference 9.

As for the transferability of semiempirical pseudopotential, Nakayama[7] calculated the charge transfer of $(AlAs)_1/(GaAs)_1$ monolayer superlattice by using both semiempirical ($\alpha = 1.15$) and *ab initio* pseudopotential. In both cases, the charge transfer occurs from AlAs layers to GaAs layers through interface. The obtained total charge transfer is 0.93% and 1.22% of the average charge density for the semiempirical pseudopotential and *ab initio* pseudopotential, respectively. This 0.29% difference contributes about 50 meV in the offset value under a simple electrostatic estimation. From the above observations, it is concluded that the present semiempirical pseudopotential method is adequate and a practical method to consider the electronic structure of an excited state.

In the present calculation a plane-wave basis set is included up to 4.41 Ry in kinetic energy. Due to this small cutoff value, we can calculate rather large systems which contain about 150 atoms in unit cells by the use of semiempirical pseudopotential.

The obtained energy gaps of bulk GaAs and InAs using the present semiempirical pseudopotentials, are 1.42 and 0.42 eV, respectively, which are 0.1 eV smaller than the experimental values of 1.52 and 0.52 eV. To estimate the real energy gap from the calculated value, we add 0.1 eV to the calculated energy gap:

$$E_g^{\mathrm{real}} = E_g^{\mathrm{calc}} + 0.1 \text{ eV} . \tag{1}$$

The semiempirical pseudopotential used in this study has the form

$$V(\mathbf{q}) = -\frac{Z_V}{q^2} \frac{\cos(a_1 q) + a_2}{1 + a_2} \exp(a_3 q^4) . \tag{2}$$

Each parameter of the potentials is given in Table II.

TABLE II. Parameters of semiempirical pseudopotentials.

	Z_V	a_1	a_2	a_3
Ga	3	1.2700	0.455 60	0.007 050
In	3	0.9491	−0.127 81	−0.010 591
As	5	1.0448	0.166 24	−0.015 120

These values are the same as those used by Nakayama *et al.*[6,7] and Taguchi *et al.*[12]

III. CALCULATED RESULTS AND DISCUSSIONS

A. Determination of the bond length of inserted InAs

To determine the bond length of inserted InAs, we calculated the total energy of $(\text{InAs})_1/(\text{GaAs})_n$ $(n=1-15)$ superlattice, and searched for the value of bond length which minimizes the total energy. Figure 3 gives the ratio between the bond length of InAs and that of GaAs, $d(\text{InAs})/d(\text{GaAs})$. As seen in Fig. 3, the obtained ratio $d(\text{InAs})/d(\text{GaAs})$ is about 1.12 and almost independent of GaAs thickness n. This gives a bond length of 2.55 Å between In and As atoms. This value is slightly shorter than that of bulk InAs. Thus in the following calculations, we set the bond length of InAs to 2.55 Å.

B. Estimation of sufficient thickness of superlattice model

To estimate the sufficient thickness of the $(\text{InAs})_1/(\text{GaAs})_n$ superlattice model, we calculate the n dependence of the energy gap. The obtained results are shown in Fig. 4. As seen in Fig. 4, for $n>40$ the energy gap saturates to the value of 1.47 eV and changes only slightly. Thus we adopt the $(\text{InAs})_1/(\text{GaAs})_{41}$ superlattice model to calculate the InAs(GaAs) monomolecular-plane system.

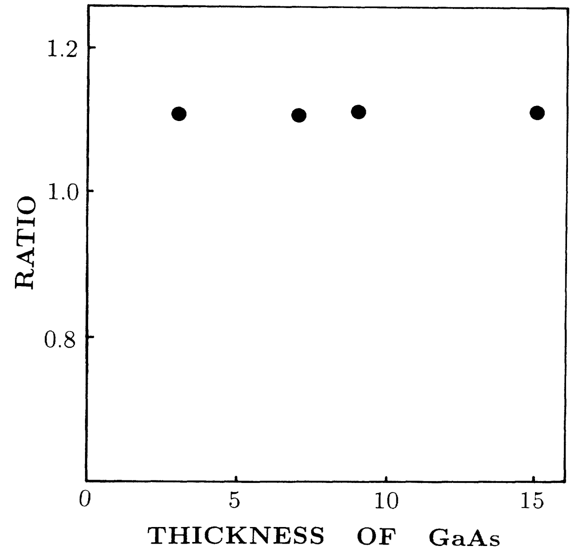

FIG. 3. Ratio between the bond length of InAs and that of GaAs plotted as a function of GaAs thickness n.

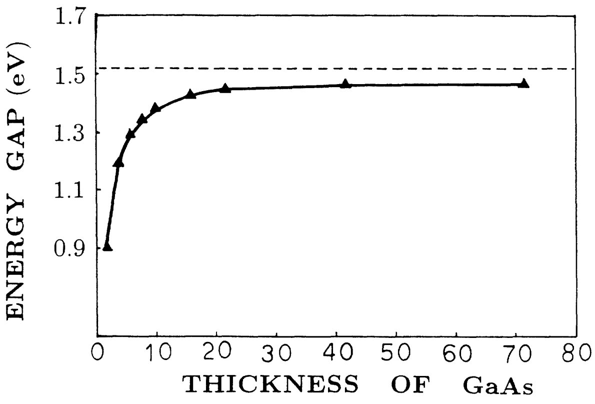

FIG. 4. Energy gap of $(\text{InAs})_1/(\text{GaAs})_n$ superlattice model plotted as a function of GaAs thickness n. The dashed line indicates the bulk GaAs band gap.

In the InAs(GaAs) monomolecular-plane system, the obtained energy band-gap value is 1.47 eV, which is 50 meV smaller than the bulk GaAs value. In the photoluminescence experiment, the measured photoluminescence peak related to the InAs monomolecular plane is about 40 meV smaller than that related to the bulk GaAs exciton edge.[1]

In the following section, we also calculate the system which consists of two InAs monomolecular planes separated by N-monolayer-plane GaAs (see Fig. 5). To calculate this structure, we adopt the $(\text{InAs})_1/(\text{GaAs})_N/(\text{InAs})_1/(\text{GaAs})_{41}$ periodic superlattice model.

C. Calculated total charge density

Table III gives the calculated total charge density between In and As layers, and that between Ga and As layers. In the system with no strain, charge transfer occurs from the In layer to the Ga layer. This direction is expected from the Phillip's electron negativity that Ga and In values are 1.13 and 0.99, respectively. However, the strain changes the direction of charge transfer. This charge transfer is explained as follows. Under the existence of the strain, the distance between In and As layers is larger than that between Ga and As layers. Consequently, without the charge transfer, valence charge density between In and As layers has a smaller value than that between Ga and As layers. Thus, the electron-

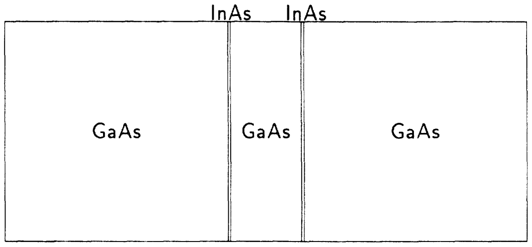

FIG. 5. Structure of a two-monomolecular-plane system, $[\text{InAs}]_2(\text{GaAs})$.

TABLE III. Total charge density between In and As layers and between Ga and As layers. In the bulk GaAs, there are four electrons between Ga and As layers.

	No strain	With strain
In-As	3.9433	4.0006
Ga-As	4.0000	4.0000

electron Coulomb interaction yields a charge transfer from the Ga layer to the In layer. In real strained systems, charge transfer is determined by the competition between Coulomb interaction induced by the strain and the electron negativity.

D. Calculated level charge density

We have calculated the level charge density at the conduction-band bottom and valence-band top, which is averaged in the plane parallel to the interface, to study the character of electrons and hole. Figure 6 gives the averaged calculated level charge density of the $(\mathrm{InAs})_1/(\mathrm{GaAs})_{71}$ superlattice system. Here, the upper line corresponds to electrons and the lower line corresponds to holes. As seen in Fig. 6, both electrons and holes are localized around the inserted InAs plane, within 200 and 120 Å, respectively. Thus it can be expected that the exciton state is localized along the *c* axis. These results successfully explain the marvelously strong intensity of experimental photoluminescence and its polarization parallel to the plane. The two-dimensional energy dispersions of the conduction-band bottom and valence-band top are almost the same as that of bulk GaAs, but located slightly lower than the bulk GaAs conduction band and slightly higher than the bulk GaAs valence band, respectively. Thus the effective mass values of hole and electron in this system seem to be closed to those in the bulk GaAs.

We also calculate the $(\mathrm{InAs})_1/(\mathrm{GaAs})_{15}$ superlattice system by the *ab initio* pseudopotential method to check the transferability of the semiempirical pseudopotential. Also, in this calculation the characters of the valence-band top and conduction-band bottom are localized around the inserted InAs planes are the same as the results obtained by the semiempirical one.

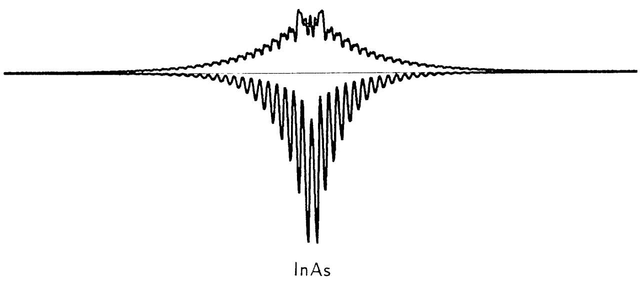

FIG. 6. Calculated averaged level charge density of InAs(GaAs) monomolecular-plane system. The upper line corresponds to the electron state and the lower line corresponds to the hole state.

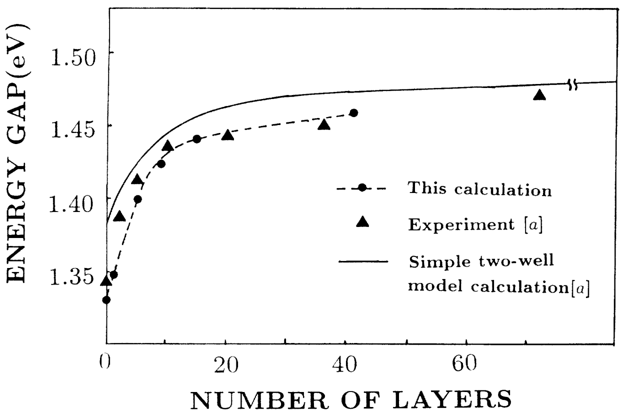

FIG. 7. Calculated energy gaps as a function of N for a system with two InAs monomolecular planes separated by N monolayers of GaAs, $[\mathrm{InAs}]_2(\mathrm{GaAs})_N$. *a* denotes Ref. 1.

As stated above, in the InAs(GaAs) monomolecular-plane system, the characteristics of electrons and holes are very similar to in the ordinary single quantum-well system. An InAs monomolecular plane behaves like a kind of single quantum well, in the sense that both electrons and holes are attracted around it.

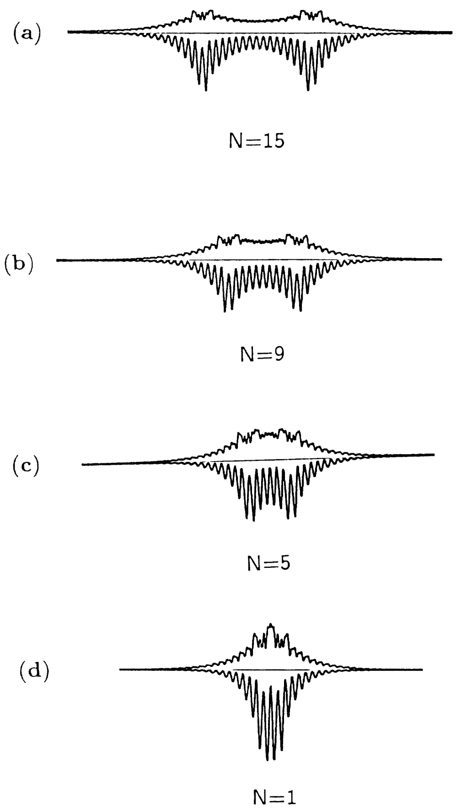

FIG. 8. Calculated averaged level charge density of a system with two InAs monomolecular planes separated by N monolayers of GaAs, $[\mathrm{InAs}]_2(\mathrm{GaAs})_N$. The upper line corresponds to the electron state and the lower line corresponds to the hole state. (a) $N=15$, (b) $N=9$, (c) $N=5$, and (d) $N=1$.

E. Two InAs monomolecular planes

We have calculated the electronic structure of two InAs monomolecular planes separated by N monolayers of GaAs. In Fig. 7, the calculated energy gaps are plotted as a function of GaAs thickness N, where experimental results of photoluminescence energies and simple two-well calculations are also plotted. As seen in Fig. 7, as N increases from 0 to 41, the energy gap changes from 1.35 to 1.46 eV, and the results of this calculation fit the experimental data very well, although we do not take into account the excitonic effect. The system with $N=0$ corresponds to 2-monolayer-thick InAs in GaAs. The energy approaches the values for the monomolecular-plane system when N increases.

Sato *et al.* calculated this N dependence of energy gap by the simple two-well model approach[1] (see Fig. 7). Their calculated results also reproduce experiments well. In their calculations, they used the bulk GaAs effective masses in the InAs monomolecular wells and adopted the conduction-band offset ratio of 85% which is the same as the bulk offset value between GaAs and InAs. It is interesting that the simple square-well model works well even in the InAs monomolecular well. In the case of the $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ superlattice it seems not to work well. This is because both GaAs and InAs are direct-band-gap materials, thus the mixing of Γ point and X point, which is very important in the $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ superlattice, does not affect the energy gap.

The calculated level charge densities, averaged in the x-y plane are given in Fig. 8 for $N=1$, $N=5$, $N=9$, and $N=15$. The degree of localization around the InAs monomolecular plane decreases as N increases. At small N value, the wave function "feels" an attraction from two InAs potentials, which results in the small energy gap of the system. However, at large N value, only one InAs plane affects the wave function. Thus the energy gap approaches the monomolecular-plane value 1.46 eV, for large N.

IV. SUMMARY AND CONCLUDING REMARKS

We have calculated the electronic structure of the InAs(GaAs) monomolecular-plane–host-crystal system by a self-consistent pseudopotential method. The bond length between inserted In and As atoms is slightly shorter (2.55 Å) than that of bulk InAs. In this system, electrons are transferred to the InAs layer across the interface as a result of the electron-electron interaction arising from interfacial strain. Both electrons and holes are localized around the inserted InAs plane. This result successfully explains the observed intense photoluminescence and polarization parallel to the interface. Thus, the InAs(GaAs) monomolecular-plane system is expected to be a promising material for optical devices. In the system composed of two InAs monolayer planes separated by N monolayers of GaAs, electrons and holes are strongly localized around the two inserted InAs planes. The degree of the confinement decreases as N becomes large. The calculated band gap as a function of N is in good agreement with the experimental results.

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