Chemical and electronic properties of Ga on the InP(100) surface

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The Stranski-Krastanov growth mode of Ga on the InP(100) surface is reexamined by electron-energy-loss spectroscopy and other surface-sensitive techniques. The formation of GaP on top of the InP surface as the result of the Ga-In exchange reaction is postulated from the experimental evidence, and the energy-band discontinuity between InP and GaP is estimated.

The bonding, chemical reaction, and interface formation of group-III elements on GaAs surfaces have been an interesting area of study during the last years. Recently, the investigation of the same subject on other III-V compound semiconductor surfaces, especially InP, has attracted some attention. However, most of the works have focused on the (110) cleaved surface. Houzay *et al.* presented the first detailed investigation of Ga-InP(100) interface formation at room temperature under ultrahigh-vacuum conditions.[1,2] They proposed a Stranski-Krastanov growth mode in addition to the Ga-In surface exchange reaction based upon their low-energy electron diffraction (LEED), ultraviolet photoemission spectroscopy (UPS), and Auger electron spectroscopy (AES) measurements. However, all these techniques could only provide indirect evidence of Ga island formation. In their paper, transmission-electron-microscopic observations show clearly liquid or amorphous islands, but only at very high coverage, i.e., 256 monolayers (ML) of Ga. The question of whether Ga islands really exist at the earlier stage of deposition still needs to be investigated carefully. In this work, we confirm the Stranski-Krastanov growth mode by electron-energy-loss spectroscopy (EELS) measurements and suggest that a thin GaP overlayer on top of the InP forms as the result of a Ga-In exchange reaction. The electronic states at the interface between this thin GaP layer and the InP substrate are also discussed.

The work was done on a VG ESCALAB-5 electron spectrometer facilitated with LEED, AES, x-ray photoemission spectroscopy (XPS), and UPS. The base pressure of its vacuum chamber was better than 2×10^{-8}Pa.

The sample was an n-type Sn-doped InP(100) single-crystal wafer chemico-mechanically polished and chemically cleaned by the ordinary device process. After being loaded into the vacuum chamber, the sample surface was repeatedly treated by 600-eV argon-ion sputtering for 5 min followed with 320°C annealing for one hour until a sharp (4×2) LEED pattern could be observed and no trace of C,O, or other impurities showed in its Auger spectrum. The gallium source was produced by electrically heating a tungsten-wire basket which contained the high-purity metallic gallium. The tungsten wire was thoroughly degassed before each evaporation run. The deposition rate and the thickness of the gallium overlayer were calibrated by measuring the peak intensities of the Ga $2p$ and Si $2p$ XPS signals as a function of evaporation time in the case of Ga deposition on the top of a silicon substrate. The deposition rate used in our experiment as the heating current was fixed was estimated to be approximately 1 Å/min.

The evidence of uniformly layered growth of Ga at the initial stage of deposition was illustrated by the combined results of UPS and EELS measurements. A series of UP spectra excited by the He I light source for different coverages of Ga on the InP(100)(4×2) surface is shown in Fig. 1. The surface-state peak labeled by S_1, which is induced by the dangling bonds of surface P atoms, decreases in intensity rapidly with the increase of Ga coverage and almost fully disappears at Ga-overlayer

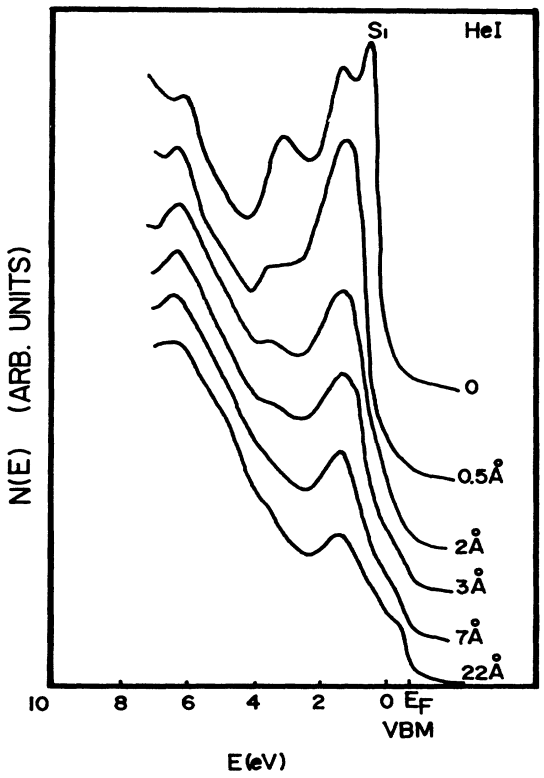

FIG. 1. The valence-band UPS for different coverages of Ga on the InP(100)(4×2) surface.

thicknesses above 1.5 Å. This characteristic is quite different from that of Ga on an InP(100) surface, where the surface-state peak S_1 still remained even if the thickness of the Ga overlayer reached several monolayers. Williams *et al.*[3] suggested that this was due to the islandlike growth of Ga on the InP(100) surface, in which the area between those Ga islands was still the undisturbed clean InP surface. But this is not the case for Ga on the InP(100) surface, where one monolayer of Ga will annihilate almost all the dangling bonds of surface P atoms.

In addition, the surface dangling bonds of In atoms are also affected by the initial deposition layer of Ga, as illustrated by the EELS results in Fig. 2. The two peaks at the loss energies of 17.9 and 18.8 eV labeled as (SE) correspond to the transitions from In $4d_{5/2}$ and In $4d_{3/2}$ core levels to the surface-exciton state induced by the dangling bonds of In atoms. The surface-exciton state is very sensitive to the chemical environment of the dangling bonds. The rapid decrease of the intensity of (SE) with the increase of the amount of deposited Ga in Fig. 2 might serve as evidence that one monolayer of Ga overlayer will affect all the surface In dangling bonds.

The above two facts verify that at the initial stage of deposition the Ga atoms are uniformly distributed on the surface until all the surface P and In dangling bonds are disturbed.

Meanwhile, the surface Ga and In exchange reaction is quite remarkable, as illustrated by core-level UPS and XPS measurements. Figure 3 shows the evolution of In $4d$ photoelectron spectra excited by He II light source after depositing different amounts of Ga. Even at a coverage of 0.5 Å, the shoulder at the lower-binding-energy side of the In $4d_{5/2}$ peak is clearly observed. The appearance of this low-binding-energy peak, which is the peak for metallic In, serves as the fingerprint of the Ga-In exchange reaction.[4] The Ga atoms replace the In atoms and combine with the P atoms to form Ga—P bonds on the surface. This has also been illustrated by XPS. In Fig. 4 the Ga $2p$ XPS peaks for different Ga coverages on the InP surface are compared with those from GaP and metallic Ga. It can be seen that at lower coverages, the Ga $2p$ peak position seems closer to that of GaP.

The formation of GaP by the exchange reaction will possibly leave Ga dangling bonds on the surface. In Fig. 2 it seems that, accompanying the decrease of the (SE) doublet, a loss peak develops at an energy of 20.2 eV, labeled as $(SE)_{Ga}$, which could be assigned to the loss mechanism related to the electronic transition from Ga $3d_{5/2}$ and Ga $3d_{3/2}$ core levels to the exciton level associated with surface Ga dangling bonds.[5] Since the energy

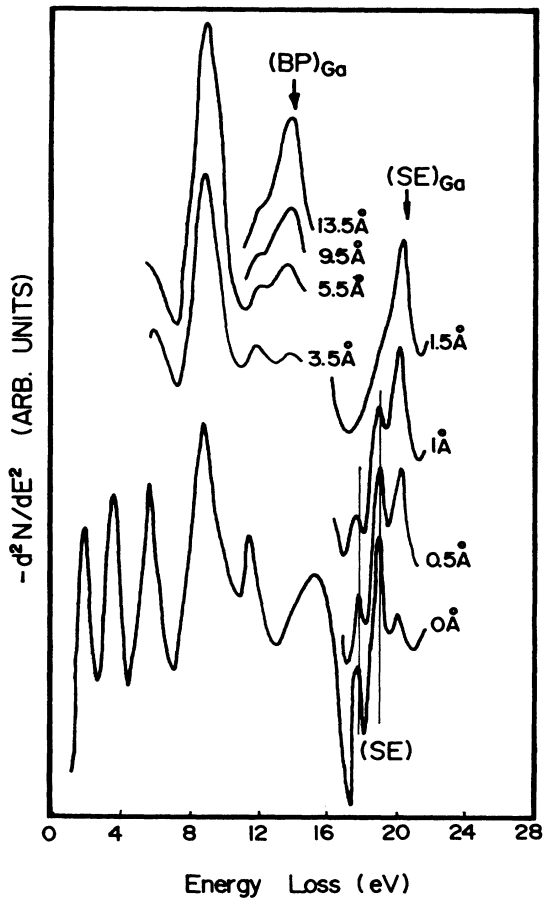

FIG. 2. ELS of the InP(100)(4×2) surface under different coverages of Ga.

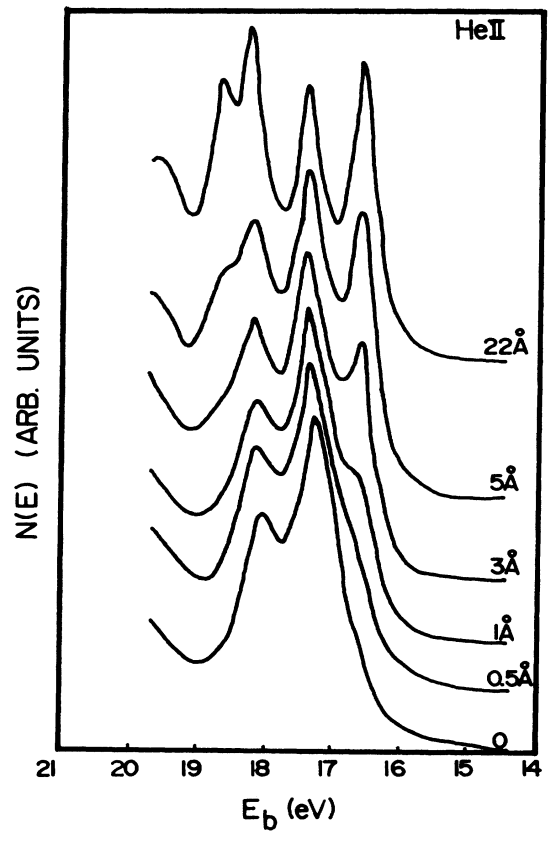

FIG. 3. The core level UPS for different coverages of Ga on the InP(100)(4×2) surface.

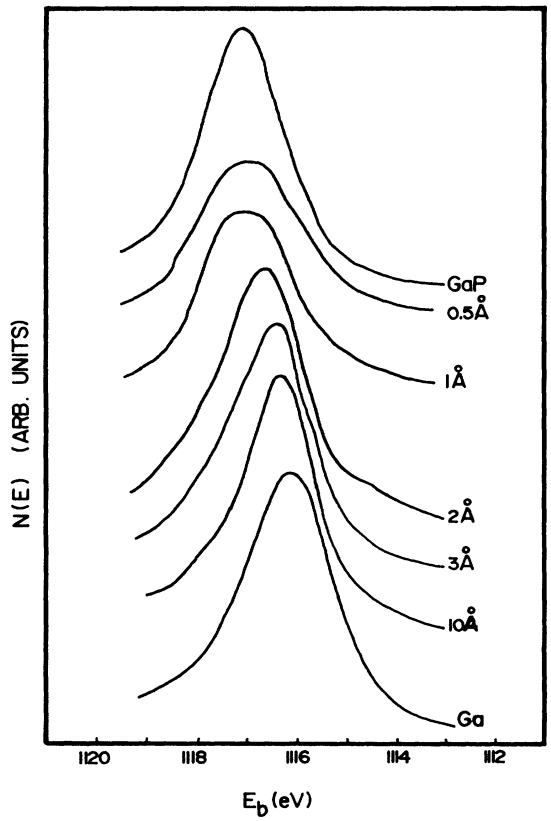

FIG. 4. XPS of Ga $2p$ at different coverage of Ga on the InP(100)(4×2) surface.

difference between Ga $3d_{5/2}$ and $3d_{3/2}$ is only about 0.45 eV, the doublet of $(SE)_{Ga}$ could not be resolved in the spectra.

The intensity of the In $4d_{5/2}$ peak from metallic In increases with the thickness of the Ga deposition layer in Fig. 3. Meanwhile, the peaks of Ga $3d_{5/2}$ and $3d_{3/2}$ can be observed after the deposition Ga overlayer is thicker than 3 Å. However, since in this measurement the Ga $3d$ peak overlaps with the In $4d_{3/2}$ peak from the InP substrate, it is difficult to determine the exact energy position of the Ga $3d_{5/2}$ peak so as to identify whether the Ga exists in the metallic form or in the compound form at the early stage of Ga deposition. But for very thick Ga overlayers, i.e., 22 Å, the Ga $3d_{5/2}$ peak appears at 18.95 eV below the valence-band maximum (VBM) of InP, which corresponds to the peak of metallic Ga. At this coverage, the In $4d$ signal from the metallic state is still very remarkable in the spectrum. This could be explained as the result of In segregation and clustering on the top of the Ga overlayer.

On the other hand, the evidence of Ga island formation could be clearly indicated by the appearance of the peak labeled $(BP)_{Ga}$ in the EEL spectrum once the thickness of the Ga overlayer is larger than 3.5 Å, as shown in Fig. 2. This gives a strong support to the island growth mode of Ga on InP beyond the first stage of the layered growth mode, since the EELS is much more sensitive in identifying the metallic island formation on III-V compound semiconductor surfaces than other surface electron spectroscopies.[6,7]

Because the surface Ga-In exchange reaction is so important from the beginning of Ga deposition to a relatively thick Ga overlayer, it seems reasonable to assume that a portion of InP on the surface is replaced by GaP. The Ga/InP interface might look like a GaP/InP (or GaInP/InP) heterostructure. If the conception of energy-band structure is still valid for such a very thin GaP (or GaInP) layer, the band discontinuity between GaP and InP could be estimated by the experimental results above. We construct the energy-band diagram at the interface of the supposed GaP/InP heterostructure as shown in Fig. 5. The binding energy of In $4d_{5/2}$ obtained from a clean InP surface by UPS in Fig. 3 is 17.25 eV. The energy distance between In $4d_{5/2}$ and the VBM of InP was found to be 16.60 eV.[8] Their difference, 0.65 eV, gives the position of Fermi level E_F with respect to the VBM. After deposition of 0.5 Å of Ga on the InP surface, the In $4d_{5/2}$ peak shifts 0.1 eV towards higher binding energy and is no longer variable at higher Ga coverages. Therefore E_F at the Ga/InP interface has to be pinned at 0.75 eV above the VBM of InP. The measured binding energies of the Ga $3d_{5/2}$ and $3d_{3/2}$ peaks in our system are 18.25 and 18.70 eV, respectively, which correspond to the metallic Ga state. For GaP, the binding energies of Ga $3d_{5/2}$ and Ga $3d_{3/2}$ would have values about 1.0 eV larger than those of metallic

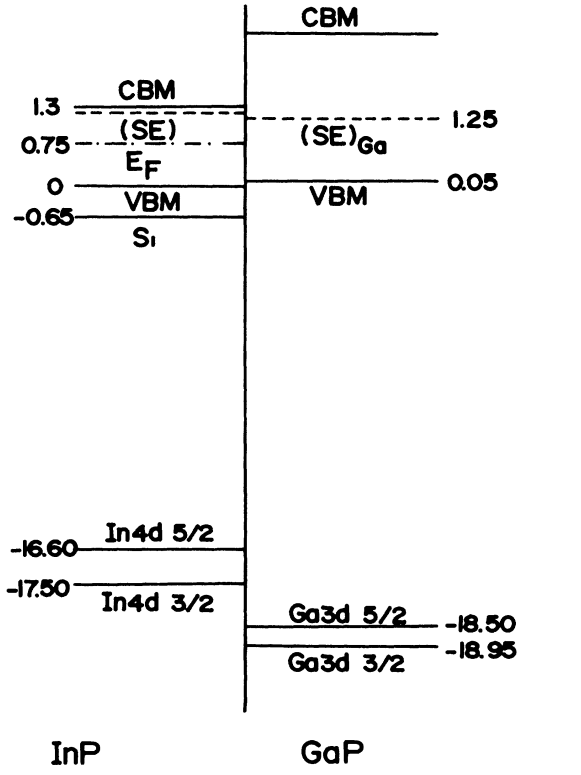

FIG. 5. Proposed energy-band diagram at the interface of GaP/InP heterostructure.

Ga, as illustrated by the comparison of the Ga $2p$ peak of GaP to that of metallic Ga in Fig. 4. So, the Ga $3d_{5/2}$ and Ga $3d_{3/2}$ core levels in GaP are located at 18.50 and 18.95 eV below the VBM of InP, respectively. The $(SE)_{Ga}$ EELS peak is at 20.2 eV, which is determined mainly by the transition between Ga $3d_{3/2}$ and the surface-exciton level of Ga.[9] Since the surface exciton is a kind of Frenkel exciton which is localized around the column-III atoms, the long-range ordering does not affect its energy-level position. Huijser *et al.*[10] found that the energy level of $(SE)_{Ga}$ is 1.2 eV above the VBM for the GaP(110) surface. The same value could be expected in our case. Finally, the VBM of GaP is estimated to be 0.05 eV above the VBM of InP. Considering the inaccuracies of the measured peak positions, the above value of the valence-band discontinuity might have an error not less than ± 0.1 eV. Roughly speaking, the VBM's of GaP and InP line up almost at the same level.

Because of the severe lattice mismatch between GaP and InP, the investigation of GaP/InP heterostructures has not attracted much attention and direct experimental data of the band discontinuity for this system are not available. Among the theoretical predictions, Tersoff[11] proposed a dipole-minimization model which gave rise to the fairly good overall agreement with the experimental band-offset data for a number of III-V–Ge and III-V–Si heterostructures.[12] The valence-band discontinuity of a fictitious GaP/InP interface predicted by Tersoff's midgap energies is 0.05 eV, which agrees well with our experimental estimation based upon such an over simplified interfacial structural model.

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