Atomic Structure of Heteroepitaxial Interface between II-VI and III-V Semiconductor

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A series of pseudomorphic (100) ZnSe/GaAs heterostructures were grown by molecular beam epitaxy on GaAs epilayers which had different As coverages of surfaces. A large variation of the interface state density was observed among the heterostructures by capacitance-voltage measurements. Transmission electron microscope observations of cross-sectional samples have revealed existence of an interface layer in the heterostructures grown on As-deficient GaAs surfaces. Analyses of dark field images and high resolution microscope images have shown that the interface layer has a structure similar to that of Ga$_2$Se$_3$ which crystallizes in a zincblende type structure with vacancies on the Ga sublattice.

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I. Introduction

Up to the present, II-VI/III-V semiconductor heterostructures have been grown mainly due to the requirement of high quality substrates for growth of II-VI semiconductor epilayers and the lack of high quality bulk crystals of II-VI semiconductors. In recent years, the growth of II-VI/III-V semiconductor heterostructures has raised a new possibility due to a significant progress in the quality of the heterostructures by utilizing advanced thin film growth techniques such as molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD). Heterojunctions of II-VI/III-V semiconductors offer a wider range of combinations of band gaps under the restriction of close lattice matching than those of conventional III-V/III-V semiconductor heterojunctions and, hence, provide an opportunity of developing a variety of new novel electronic devices. In addition, the use of this type of heterojunctions is now considered as a possible alternative way for development of light emitting devices of wide-gap II-VI semiconductors; the fabrication of p-n junctions of wide-gap II-VI semiconductor devices is known to be very difficult due to the problem of self-compensation.

For realization of II-VI/III-V semiconductor heterojunction devices, however, the preparation of stable heteroepitaxial interfaces having good electronic properties stands as a major material problem as explained in the following. Unlike conventional III-V/III-V and II-VI/II-VI semiconductor interfaces, II-VI/III-V semiconductor interfaces may lead to the formation of a number of compounds having different crystal structures due to various combinations of valences of constituent elements. For example, Ga$_2$Se$_3$ having a defect zincblende structure, GaSe having a layer structure, Zn$_3$As$_2$ having a defect fluorite structure, or ZnAs$_2$ having a monoclinic structure may form at a ZnSe/GaAs interface. The possibility of the formation of various compounds implies that atomic structures of II-VI/III-V semiconductor interfaces may vary significantly by growth conditions such as fluxes and substrate surface compositions, and, hence stable or unstable interfaces may result depending on their atomic structures.

For achieving II-VI/III-V heterojunction devices, important results have been obtained in a recent study by Qian et al. This study has demonstrated the feasibility of the preparation of ZnSe/GaAs heterojunctions whose interface state densities are comparable to those of high quality GaAs/(Al,Ga)As heterojunctions. For the preparation of these heterojunctions, the growth of pseudomorphic ZnSe epilayers on GaAs epilayers and post-growth annealing were employed. In a more recent development, as-grown ZnSe/GaAs heterostructures having interfaces with the similar quality have been obtained by growing ZnSe on As-deficient GaAs surfaces without the need for the post-growth annealing. These results suggest that highly stable ZnSe/GaAs interface structures with good electronic properties can be obtained by employing suitable growth conditions or post-growth treatments. As a possible stable interface structure, Tu and Kahn have suggested the formation of a (Ga,Se) compound layer at the ZnSe/GaAs interface in earlier studies which employed surface spectroscopic techniques. To date, however, no direct confirmation of the formation of interface compound layers in II-VI/III-V semiconductor heterostructures by either diffraction or
imaging techniques has been reported.

In this paper, we present a transmission electron microscope (TEM) study of atomic structures of (100) ZnSe/GaAs heteroepitaxial interfaces which have formed on GaAs surfaces having different As coverages. The study has shown a direct correlation between the interface electronic property and interface atomic structure with the existence of interface compound layers in heterostructures grown on As-deficient GaAs surfaces.

II. Experimental Procedure

For the study, a series of (100) ZnSe/GaAs heterostructures were grown by using a Perkin-Elmer model 430 modular MBE system. A 1.5 μm thick Be doped p-type (1.0 × 10^{23} m^{-3}) GaAs epilayer was first grown on a GaAs substrate and transferred through an ultra-high vacuum (2 × 10^{-3} Pa) tube to another growth chamber for the growth of ZnSe. Thicknesses of ZnSe epilayers are about 100 nm which is smaller than the critical thickness expected from the lattice mismatch (0.25%) between ZnSe and GaAs. Surfaces of GaAs epilayers on which ZnSe epilayers were grown were varied from As-rich to As-deficient conditions among the heterostructures by heating GaAs prior to the growth of ZnSe. The change of a surface by the heating was monitored by the observation of reflection high energy electron diffraction (RHEED) patterns. Results of analyses of the following three heterostructures are described in this paper: the sample A grown on an As-rich surface which exhibited a c(4 × 4) reconstruction structure, the sample B grown on a surface which had an intermediate As coverage and exhibited a (4 × 6) reconstruction structure, and the sample C grown on a highly As-deficient surface which exhibited a (4 × 3) reconstruction structure. The c(4 × 4) structure is known to form on an As-rich surface, while the (4 × 6) structure is normally observed on a relatively As-deficient surface\(^{10}\). The (4 × 3) structure was obtained by heating GaAs for a longer period of time than those for the other two samples without fluxes and, hence, is considered to be highly As-deficient. The (4 × 3) structure appears to result from the adsorption of residual Se vapors on the As-deficient surface. Details of the growth procedure of these heterostructures are described in other reports\(^{9,10}\).

Following the growth of the heterostructures, circular capacitors with Al metallization were fabricated by an evaporation lift-off procedure. The capacitance-voltage (C-V) measurements were performed under computer control with HP4274A and 4275A LCR meters. All data were taken at 1 MHz with a sweep rate of 0.1 V/s in the dark. The interface state density distributions were calculated by using the Terman’s method\(^{11}\). Two parameters needed for the calculation, the GaAs epilayer doping and the ZnSe layer thickness, were obtained from the C-V profiling and TEM observation, respectively. Details of the procedure of these measurements are described in other reports\(^{9,10}\).

For the TEM observation, (011) and (010) cross-sectional samples were prepared by ion thinning. Iodine ions were used at the final stage of the thinning in order to reduce damages in the samples\(^{12}\). A JEM 2000 EX electron microscope equipped with an ultra-high resolution objective lens pole-piece was used. The spherical aberration coefficient of the pole-piece is 0.7 mm.

III. Results and Discussion

Results of the measurements of interface state densities of three heterostructures A, B and C are shown in Fig. 1. By comparing interface state densities near the mid-gap, a clear trend of reduction in the interface state density is seen as the GaAs epilayer surface became increasingly As-deficient. The heterostructure C which was grown on the most As-deficient GaAs surface has the lowest interface state density comparable to those of high quality GaAs/(Al, Ga)As heterojunctions. Because of the significant reduction of interface states in the sample C, the Fermi level was found to be free to move, and the band bending spanned the entire GaAs band gap. Although the structural origin of interface states in this system is not known, results shown in Fig. 1 strongly suggest the variation of interface structures among three samples.

Dark field images and high resolution electron microscope (HREM) images of cross-sectional samples of each heterostructure were examined in order to find a difference of interface structures due to the change of the As-coverage of GaAs surfaces. The 200 dark field images of (010) cross-sectional samples were found to exhibit the most significant difference among three heterostructures. Figure 2(a), (b) and (c) are 200 dark field images of (010) cross-sectional samples of the heterostructures A, B and C, respectively. All these dark field images were taken under the identical condition; the 200 reflection was set at the exact Bragg condition, and only h00 type reflections were excited. The areas included in the images are close to edges of samples and have thicknesses of a few hundred angstroms. As seen in the images, the samples B and C surfaces show a distinct bright line at the interface between ZnSe and GaAs epilayers. These bright lines at the

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Fig. 1 Interface state density distributions of ZnSe/GaAs heterostructures A, B, and C.
interfaces are seen in all observed areas from edges to thicker parts of cross-sectional samples. The bright line of the sample C appears to be more continuous than that of the sample B. Dark field images of 200, 002 and 002 reflections also show similar bright lines at interfaces under their exact Bragg conditions. The 200 type dark field images of the sample A, on the other hand, do not show such a bright line. Some areas of this heterostructure show a bright line along the interface, but it is an extremely weak one, compared to those seen from the other two heterostructures. The difference among three heterostructures, that is, the appearance of a distinct interface bright line in the images of the heterostructures B and C and the absence of such an interface line in the images of the heterostructures A, suggests the existence of a thin layer at the ZnSe/ GaAs interfaces which have formed on As-deficient GaAs surfaces.

In order to analyze the atomic structure of the interface layer whose existence is suggested by 200 type dark field images, HREM images and dark field images of other reflections were examined. In the following, the observation of the heterostructure B is described. Similar
Fig. 3  (a) [010] HREM image, and (b) dark field image of the ZnSe/GaAs interface. In the dark field image (b), the upper side is ZnSe, and the lower side is GaAs.

results have been obtained from the heterostructure C. Figure 3(a) is a [010] HREM image of the ZnSe/GaAs interface. The image was taken at the defocusing of about $-60 \text{ nm}$ with an objective lens aperture having a diameter of $8 \text{ nm}^{-1}$. The thickness of the observed area is about $50 \text{ nm}$. In the image, a dark band with a width of about two monolayers is seen along the ZnSe/GaAs interface. This dark band is seen along the interface in all observed [010] HREM images of the sample except very thin areas close to edges of the sample. Compared to [010] HREM images, [011] HREM images do not show a clear dark band along the interface, which may be attributed to the high contrast of (111)-type lattice fringes in the later images. The appearance of a dark band suggests a certain form of modification of the interface structure from the abrupt one, but lattice fringes in HREM images show a perfect coherency between ZnSe and GaAs crystal lattices.

The observation of dark field images of (010) cross-sectional samples shows a systematic dependence of the contrast of the interface layer on the reflection used for the imaging. Under exact Bragg conditions, all 200 type dark field images as well as 420 type dark field images exhibit a bright interface line, while all 400 type and 220 type dark field images show a dark interface line. Figure 3(b) is a dark field image of the 400 reflection. The image was taken under the exact Bragg condition of the 400 reflection with the excitation of only h00 type reflections. The thickness of the observed area is about $40 \text{ nm}$ which was estimated using locations of thickness contours. In the
image, a distinct dark line is seen at the ZnSe/GaAs interface. This dark line appears at the interface in all parts of observed areas except those crossed by dark thickness contours where the interface appears as a bright line. Similar dark lines at the interface are observed in 400, 004, and 004 dark field images taken under their exact Bragg conditions.

The crystal structure factor of the 200 reflection for the zincblende structure is given by a difference of scattering factors of atoms occupying two different face centered cubic (fcc) sublattices, while the crystal structure factor of the 400 reflection is an addition of scattering factors of these two types of atoms. Considering this relation, one can give a simple explanation for the observed dark field images of the interface with the following model of the interface layer. Between ZnSe and GaAs crystals, a very thin layer having a zincblende structure exists by maintaining the coherent relation. One of the fcc sublattices is occupied by cations, i.e., Zn or Ga, and the other has anions, i.e., Se or As. Unlike the GaAs and ZnSe crystals, one of the fcc sublattices in the thin layer has a high concentration of vacancies. Because of vacancies in one of the fcc sublattices, the crystal structure factor of the 200 reflection of the thin layer becomes much greater than those of GaAs and ZnSe which are very small due to nearly equal values of scattering factors of constituent atoms. The thin layer, therefore, will appear with a brighter contrast in the 200 dark field image. In the 400 dark field image, on the other hand, the thin layer will appear as a dark line as a result of the smaller crystal structure factor than those of GaAs and ZnSe. Similar explanations can be given to 420 and 220 type dark field images.

There are a number of other possible models of the interface layer, but it is difficult to explain observed images based on those models. If the interface layer is simply an intermixed layer of GaAs and ZnSe, no bright nor dark line are observed in dark field images because of very close values of atomic scattering factors of Zn, Ga, As and Se atoms. If, on the other hand, the interface layer is an area where bond lengths and bond angles largely differ from those of GaAs and ZnSe, both 200 and 400 dark field images are expected to show dark contrast along the interface under exact Bragg conditions. It is also difficult to explain these dark field images by assuming the presence of Ga or Se clusters at the interfaces.

As described earlier, the study by Tu and Kahn(8) has suggested the formation of a (Ga, Se) compound layer at the ZnSe/GaAs heteroepitaxial interface. One of the stable phases of (Ga, Se) compounds, Ga$_2$Se$_3$, is known to have a structure identical to that suggested by the present observation(5). It has zincblende structure, and one third of Ga sites are left as vacancies. As a result of these vacancies, the lattice parameter of Ga$_2$Se$_3$ is about 5% smaller than those of GaAs and ZnSe. Based on the model of a thin Ga$_2$Se$_3$ layer, which is coherently inserted into the ZnSe/GaAs interface, intensities of 200 and 400 dark field images are calculated. Figure 4 schematically illustrates the model. The calculations are made based on the two beam dynamical diffraction theory with the column approximation. Figure 5(a) and (b) are calculated intensity profiles of 400 and 200 dark field images, respectively. The thickness of the crystal is assumed to be 40 nm and the incident beam is set at the exact Bragg condition in both cases. As seen in the figures, the calculations are in good agreement with observed images despite the use of simple approximations. The profile of the 200 dark field image shows a bright contrast of the Ga$_2$Se$_3$ layer, while the 400 dark field image has a drop of the intensity at the interface layer.

As explained in Introduction, a number of compounds may form at the ZnSe/GaAs interface besides Ga$_2$Se$_3$. If we compare thermodynamic and crystal structure data of these compounds, only Ga$_2$Se$_3$ is found to form as a stable structure at the ZnSe/GaAs interface. In the crystal of Ga$_2$Se$_3$, Ga and Se atoms form a zincblende lattice similarly to II-VI and III-V semiconductor crystals, although one-third of Ga sites are left as vacancies. Therefore, Ga$_2$Se$_3$ can form a coherent layer between ZnSe and GaAs crystals. Formation of other compounds, on the other hand, is likely to lead to destruction of a coherent interface or to a highly distorted coherent interface because of the greater deviation of their crystal structures from the zincblende structure. Another indication of a good adaptability of the crystal structure of Ga$_2$Se$_3$ to those of GaAs and ZnSe is found in the fact that, among possible interface compounds in the ZnSe/GaAs heterostructure, only Ga$_2$Se$_3$ can form complete solid solutions with GaAs and ZnSe, while other compounds such as Zn$_3$As$_2$ are known to be almost immiscible to GaAs and ZnSe(13)(14). Heat of atomization,
which is one of the most direct thermodynamic data of strength of chemical bonds in compounds, also suggests that Ga$_2$Se$_3$ can form as a stable interface layer\cite{15,16}. The heat of atomization of Ga$_2$Se$_3$ is 1561 kJ/mol at 298 K which is comparable to those of ZnSe and GaAs, while Zn$_2$As$_3$ has a considerably lower value, 1000 kJ/mol. The high thermodynamic stability of Ga$_2$Se$_3$ despite the presence of vacancies is explained by the fact that vacancies are introduced into the structure in order to accommodate a mismatch between valences of constituent elements namely, Ga and Se, and the coordination number of the zincblende structure. Therefore, we can find that the interface model suggested by the present study is also supported by thermodynamic and structure properties of bulk forms of compounds. It should be pointed out, however, that no direct information on the composition of the layer can be obtained from the present TEM analysis. It is then possible to assume that the interface layer may be ternary or quarterary compounds containing Zn and/or As atoms.

Finally, we would like to point out an opportunity of investigation of an important problem which results from the present study. According to earlier studies, Ga$_2$Se$_3$ is known to form both ordered and disordered phases with a transition temperature around 973 K\cite{17}. In the high temperature phase, vacancies are distributed randomly on the Ga sublattice, while they form an ordered arrangement on the same sublattice in the low temperature phase. The arrangement of vacancies in the crystal, on the other hand, is believed to have a direct influence on its electronic properties because their presence results from the mismatch described above. Results shown in Fig. 1, therefore, suggest that interface layers in the sample B and C have vacancy ordering of a certain degree. We believe that the direct observation of the vacancy ordering in interface layers will provide an important insight of the correlation between electronic properties and atomic structures of II-VI/III-V heteroepitaxial interfaces.

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