PHYSICAL REVIEW B **72**, 121307(R) (2005)

Polarized light emission from antiphase boundaries acting as slanting quantum wells in GaP/InP short-period superlattices

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(Received 15 June 2005; published 23 September 2005)

Optical properties of anti-phase boundaries (APBs) in monolayer superlattices of GaP/InP are studied. Determining selectively the arrangements of In and Ga atoms around APBs by cross-sectional scanning tunneling microscopy, it is found that atomic layers of InP on $(\bar{1}11)$ and $(\bar{1}10)$, sandwiched between the domains of superlattices, are formed on APBs. Polarized cathodoluminescence spectroscopy in a transmission electron microscope suggested that the InP layers act as quantum wells oriented on a slant with respect to the substrate and they emit light linearly polarized parallel to the layers.

DOI: 10.1103/PhysRevB.72.121307 PACS number(s): 78.67.De, 68.35.Ct, 68.37.Ef, 78.60.Hk

Crystalline structures in nonequilibrium states such as superlattices (SLs) and quantum wells (QWs), that may possess many useful properties,[1] can be produced in semiconductors, spontaneously or artificially, by modern crystal-growth techniques, i.e., metalorganic chemical-vapor deposition (MOVPE), etc. During the growth, structural imperfections, such as defects [e.g., anti-phase boundaries (APBs), stacking faults, etc.] and composition modulation, are frequently formed, and they can affect the electronic properties in device products made of the semiconductors. For example, atomistic structure of imperfect short-period SLs has been intensively examined.[2–4] However, such structure has not been fully verified due to experimental difficulties. This paper demonstrates that they can be determined quantitatively by cross-sectional scanning tunneling microscopy (XSTM) combined with polarized cathodoluminescence (CL) spectroscopy in a transmission electron microscope.

Here atomistic structure in a short-period SL structure grown spontaneously in GaInP alloys,[5] as well as in other group III-V[6] and II-IV[7] ternary semiconductor alloys, are studied. The alloy is comprised of monolayer SLs of $Ga_{(1+h)/2}In_{(1-h)/2}P/Ga_{(1-h)/2}In_{(1+h)/2}P$ along $[\bar{1}11]$ and $[1\bar{1}1]$,[5] where the order parameter h can be controlled by varying growth conditions. APBs, at which the sequence of Ga-rich and In-rich layers is 180° out of phase,[8] are inevitably introduced during the spontaneous growth of such SLs, and emission lines with photon energies lower than the band gap energy Eg, showing signatures of quantum confinement, are observed in the SLs including APBs. The origin of this emission has been studied by optical spectroscopy with high spatial resolution combined with transmission electron microscopy (TEM) (see Refs. 6–8 and references therein). With some experimental[11] and theoretical[12] results, an atomic structure of the origin was conjectured; it was associated with APBs. On the contrary, another experiment suggested that the emission is related to defects except APBs.[9,10] The reason for the contradiction is that those workers could not obtain experimentally structural data of the APBs at an atomistic level. The atomic structure of APBs was hardly determined with TEM images on which a number of APBs expanding three dimensionally are projected. Their nature was also examined by XSTM,[13,14] even though it was not fully explored. This paper suggests that the low-energy emission arises from QWs grown spontaneously on APBs. The arrangements of In and Ga atoms around APBs were observed selectively by XSTM, and atomic layers of InP on APBs, sandwiched between SLs, were observed. The optical data obtained by polarized CL spectroscopy were consistently explained with the model that the InP layers on APBs act as QWs and they emit light linearly polarized parallel to the layers. These results may help to obtain a comprehensive insight into atomistic structures of imperfections in nonequilibrium structures as well as to explore sources of such imperfections.

The sample was an undoped $Ga_{0.5}In_{0.5}P$ layer (1 μm thick) on a GaAs substrate grown by MOVPE (the growth temperature of 650 °C, growth rate of 0.4 nm/s, III/V ratio of 370). The substrate was 2° off from (001) towards $[\bar{1}10]$, so SLs along $[\bar{1}11]$ were mainly formed.[15] A small chip of the sample was installed into an ultrahigh vacuum (UHV) scanning tunneling microscope (JEOL, JST-4500T), and then cleaved at a UHV of 1×10^{-8} Pa so as to make a clean (110) surface. A W tip etched electrochemically was approached on a GaInP SL with a UHV scanning electron microscope.[16] XSTM images were obtained at room temperature by the constant-current mode (a set current of about 100 pA). A sample voltage of about +3 V was used so as to image the empty-state density associated with In and Ga atoms. Polarized CL spectra and TEM images were obtained simultaneously[17] from a (110) cross section (about a few hundred nm thick) of the sample, at the temperature of about 20 K. A beam of 80 keV electrons was used for fear of varying the atomistic structure of GaInP SLs.[18] The probe size of a beam for the spectroscopy was about 200 nm, and the spatial resolution was estimated to be about 350 nm.[19] The effect of magnetic field in the microscope (about 1 T) on p-CL spectra is believed to be negligible for GaInP SLs.[20]

Figure 1(a) shows a XSTM image of GaInP SLs. A centered rectangular net was observed [Fig. 1(c)]. The diamond in Fig. 1(c) denotes a primitive mesh unit of the $c(2\times2)$ structure; the length of a side is about 6.9 Å, and the obtuse angle is about 110°. A GaAs surface on the same specimen was subsequently examined, and the well-known p(1×1) structure[21] was observed (not shown). Analyses of the

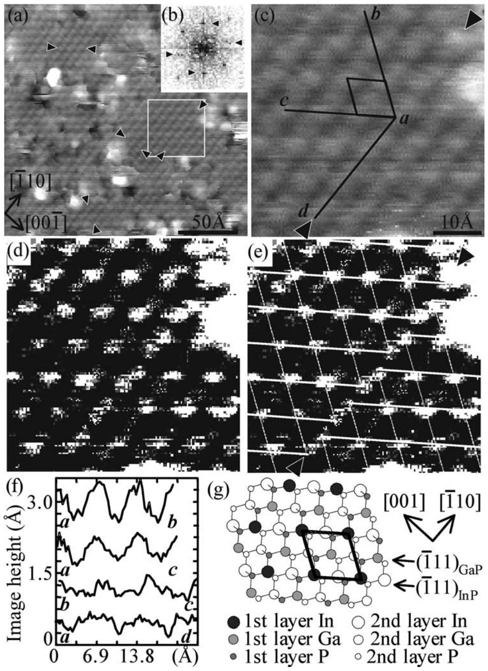

FIG. 1. (a) An empty-state image of GaInP SLs. The image is not filtered or artificially enhanced in any way. APBs are extended along the atomic rows indicated by the arrows. (b) The power spectrum of the fast Fourier transform (FFT) of (a). (c) A zoom-in view from the square region in (a). (d) The areas where the image heights are in the range from (x−0.1) Å to (x+0.1) Å in (c), in which x is the image height at *a*. (e) The bright areas in (d) arrange on diperiodic nets. (f) Height profiles along (*a*), (*b*), (*a*)–(*c*), (*b*)–(*c*), and (*a*)–(*d*) in (c). (g) The corresponding model for GaInP SL.

XSTM images revealed that the $c(2\times2)$ mesh unit is defined by two fundamental translation vectors along $[1\bar{1}2]$ and $[\bar{1}12]$. It is believed that the heights on XSTM images of GaInP SLs are determined by two factors, i.e., the difference of the bond length for In–P to that for Ga–P and the band offset at the InP/GaP interface,[13] and so the height of the *n*th In layer, nearby the surface, would be higher than that of the *n*th Ga layer on empty-state images. Figure 1(g) shows the corresponding model of a SL. The bright dots in Fig. 1(c), that have the same height as the dot at *a*, represent In atoms in the first layer [Fig. 1(d)]. The first In layer is about 0.4 Å higher than the first Ga layer [(*b*)–(*c*) in Fig. 1(f)], and the distance from the first In layer to the second In layer (about 0.6 Å[22]) is smaller than that to the second Ga layer (about 0.8 Å) [(*a*)–(*c*) and (*a*)–(*b*) in Fig. 1(f)]. The arrangement of In atoms in the first layer was also observed on an image of the inverse fast Fourier transform (FFT) of the spots marked by the arrows in Fig. 1(b) (not shown). Similar $c(2\times2)$ structures were observed on filled-state images,[13,14] and a bright dot on the net points was explained as a topmost P atom bonded to two In atoms.[13]

APBs were observed on XSTM images. For example, as shown schematically in Fig. 1(e), the sequence of In rows along $[1\bar{1}2]$ (as a guide, see the solid lines) was 180° out of phase at the atomic row, along $[\bar{1}10]$, indicated by the arrows. The row did not consist of the sequence of In–Ga-In–Ga … but that of In–In … in the first layer [(**a**)–(**d**) in Fig. 1(f)]. APBs were extended along $[1\bar{1}2]$, [001], $[\bar{1}10]$, and $[\bar{1}12]$ [e.g., Figs. 1(a) and 2(c)], and about half of APBs consisted of single In rows of the sequence of In–In … in the first layer [e.g., Figs. 1(d) and 2(e)]. The other APBs consisted of single Ga rows of the sequence of Ga–Ga … in the first layer [e.g., Fig. 2(d)]. As shown later, TEM suggested that many planar segments of APBs are nearly perpendicular to (110). A single In (or Ga) row along $[1\bar{1}2]$, [001], $[\bar{1}10]$, or $[\bar{1}12]$ would be interpreted as the cross section of an atomic layer of InP (or GaP) lying on $(\bar{1}11)$, $(\bar{1}10)$, (001), or $(1\bar{1}1)$, respectively.

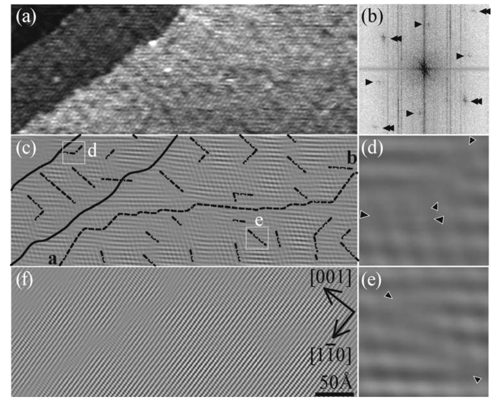

FIG. 2. (a) A low-magnified empty-state image, in which the contrast is artificially enhanced, and (b) the corresponding FFT power spectrum. (c) The image of the inverse FFT of the spots marked by the single arrows in (b), showing up In atoms in the first layer. The solid and broken curves denote monolayer-height (about 2 Å) steps and APBs, respectively. (d) and (e) Zoom-in views from the square regions in (c); (d) an APB consists of single Ga rows along $[1\bar{1}2]$ and $[\bar{1}10]$, and (e) an APB consists of an single In row along [001]. (f) The image of the inverse FFT of the spots marked by the double arrows in (b), showing up both In and Ga atoms in the first layer.

A wide area of 200×80 nm^2 was observed by XSTM, and the data[23] showed that the alloy consists of small domains (a size of 5–10 nm) of SLs with $h\approx1$ [e.g., Figs. 1(a) and 2(c)]. The domains of similar size occupied about 75%±10% of the observed area, so the order parameter was, on average, estimated that $h=0.5\pm0.2$. They were bounded by APBs [e.g., Figs. 1(e), 2(d), and 2(e)] and disordered zones, in which In and Ga atoms are distributed randomly, about 2–3 nm in width [e.g., Figs. 1(a) and 2(c)]. Most APBs were rather short (2–10 nm), while an APB was extended, nearly along $[1\bar{1}1]$, through the observed area [e.g., the broken curve along (**a**)–(**b**) in Fig. 2(c)]. The total length of the single In rows along $[hkl]$ ($hkl=1\bar{1}2$, 001, $\bar{1}10$, or $\bar{1}12$), $l_{[hkl]}$, was estimated, and $l_{[1\bar{1}2]}:l_{[001]}:l_{[\bar{1}10]}:l_{[\bar{1}12]}\approx8:11:4:3$. Stacks of In (or Ga) rows, i.e., aggregations of InP (or GaP), were not observed. Also, changes of a periodic stack of group III atomic rows except APBs, such as stacking faults and dislocations, were not observed [e.g., Fig. 2(f)].

Figure 3(a) shows a TEM image of the specimen characterized by *p*-CL spectroscopy. No extended defect except

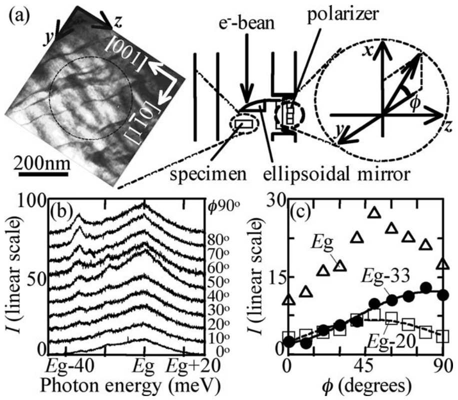

FIG. 3. (a) The experimental setup for polarized CL spectroscopy. The left figure shows a dark-field TEM image of a specimen obtained from a SL reflection. The encircled area is characterized. A CL light emitted from the specimen is reflected on an ellipsoidal mirror and the reflected light is transmitted in a linear polarizer. The transmission direction of the polarizer for electric field is determined by the rotation angle ϕ. Then, the transmitted light is collected into a charge coupled device detector through a monochromator. (b) Polarized CL spectra for various ϕ. (c) CL intensities vs ϕ. The solid or broken curve is a calculated CL intensity for the QW on $(\bar{1}10)$ or $(\bar{1}11)$, respectively.

APBs was observed. Dark black bands extended nearly along $[1\bar{1}1]$ were APBs, and the geometry of a band was similar to that of the long-extended APB on XSTM images. Light gray bands nearly along [001] were presumably associated with the short APBs, as well as disordered zones, observed by XSTM. Since many parts of the bands were narrow, many planar segments of APBs were nearly perpendicular to (110), in the thin TEM specimen. The TEM specimen emitted CL light with photon energy of $Eg=1.90$ eV [Fig. 3(b)], due to the band-to-band transition in SLs. The order parameter was estimated that $h=0.47$ with an empirical formula,[24] and the estimated value was comparable to the XSTM data. Similar TEM and CL data were obtained from any area in the specimen. The structural nature of the TEM specimen was, therefore, the same as the XSTM specimen, at a mesoscopic scale.

The TEM specimen emitted low-energy CL light with photon energies of $Eg-20$ meV and $Eg-33$ meV [Fig. 3(b)]. The low-energy CL light, as well as the CL light with Eg, were polarized in (110) [Fig. 3(c)]. The intensity of the low-energy CL light with $Eg-20$ meV was a maximum (about 7 in an arbitrary unit) at about $\phi=50°$, similar to that of the CL light with Eg. This means that the light was linearly polarized along $[1\bar{1}2]$.[25] On the other hand, the intensity of the low-energy CL light with $Eg-33$ meV was a maximum (about 12) at about $\phi=90°$. The light was linearly polarized along [001]. As a result, the low-energy CL light with $Eg-20$ meV or $Eg-33$ meV was, respectively, polarized parallel to the planar segments on $(\bar{1}11)$ or $(\bar{1}10)$ of APBs. Since APBs expand two dimensionally, the total area of the planar segments of APBs observed as single rows along $[hkl]$ on XSTM images is, as an approximation, proportional to $l^2_{[hkl]}$. The ratio between the total area of the planar segments on $(\bar{1}11)$ and that on $(\bar{1}10)$, $l^2_{[1\bar{1}2]}/l^2_{[001]} \approx 64/121$, was comparable to the ratio between the maximum intensity of the low-energy CL light with $Eg-20$ meV and that with $Eg-33$ meV, $7/12$. These results support that the low-energy CL light with $Eg-20$ meV or $Eg-33$ meV, respectively, correlates with the planar segments on $(\bar{1}11)$ or $(\bar{1}10)$ of APBs. Similarly, the planar segments on (001) and $(1\bar{1}1)$ of APBs might emit low-energy CL light, but this emission would be scarcely observed since the total areas of the planar segments were rather small.

It has been proposed that the low-energy emission arises from disk-like InP layers on APBs acting as QWs, by means of magneto μ-photoluminescence measurements by applying the magnetic field in different directions with respect to the average extension direction of long-extended APBs,[11] and a theoretical study of the disk-like InP layers has revealed that the model explains various properties of the low-energy emission.[12] Based on the InP QW model, the ϕ-dependent intensity of the lights emitted from a QW and then transmitted through an apparatus[17] for polarized CL spectroscopy was calculated,[26] with a classical QW theory.[27] The result for a QW on $(\bar{1}11)$ or $(\bar{1}10)$, respectively, explained well the ϕ-dependent intensity of the low-energy CL light with $Eg-20$ meV or $Eg-33$ meV [Fig. 3(c)]. The photon energy of the light emitted from a QW should decrease with increasing the QW thick. The thickness of a InP layer on the planar segment of $(\bar{1}11)$ or $(\bar{1}10)$ of APBs, respectively, was estimated to be 0.33 or 0.40 nm from Fig. 1(a), and the former value was smaller than the latter one. Moreover, an InP layer thinner (0.28 nm) or thicker (0.57 nm) than the $(\bar{1}11)$ and $(\bar{1}10)$ InP layers, grown artificially in a GaInP alloy, emits the light with higher ($Eg-14$ meV) or lower ($Eg-47$ meV) energy, respectively.[29] Thus the polarization, intensity, and photon energy of the low-energy CL lights, emitted from an undoped sample in the present study, were expounded with the InP QW model. Scanning near field spectroscopy combined with TEM has suggested that the low-energy emission does not correlate with APBs, since a number of low-energy lines with different energies were emitted from small areas both on and off long-extended APBs.[9,10] This paper showed that small domains of SLs bounded by APBs, that are observable by XSTM but not observed clearly by TEM, exist in the "large domains" bounded by long-extended APBs that are distinctly observable by TEM, and no defect except APBs was observed. It is theoretically expected that the photon energy of the low-energy light emitted from a disk-like InP layer depends on the size of the disk.[12] The low-energy lines observed in Refs. 9 and 10 might be emitted from small InP layers with different size, on APBs inside large domains. Atomic layers of GaP sandwiched between domains of SLs would not emit CL, as expected theoretically.[12]

Localized energy levels in InP layers sandwiched between domains of SLs may be determined by XSTM. The image heights around some APBs differed from that on domains of SLs [Fig. 2(a)], even though the cleaved surface was atomically flat. Similar mottled contrast was observed on a GaInP alloy,[30] and it was attributed to electronic and strain effects associated with fluctuations in the alloy composition.[31] The electronic states around APBs would be modified by introducing InP layers.[12] Further study, especially at low temperatures, may be necessary to explain the contrast.

In conclusion, observing distinctly the arrangements of atoms by XSTM and obtaining polarized CL spectra at a high spatial resolution, the novel atomistic structure of GaP/InP short-period SLs has been proposed; slanting QWs are formed spontaneously in the SL structure. The experimental method will be used for discovering and quantitative understanding of novel optical properties of various kinds of nanostructures.

This work was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientist (A)(2) No.15681006, 2003-2005. GaInP SLs were provided by Mitsubishi Chemical Co. I am indebted to Professor S. Takeda for use of the facilities and for fruitful discussion.

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