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Effects of Ultrathin AlAs Interfacial Layer on Photoluminescence Properties of GaInP Epilayer Grown on Ge

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**Abstract**
The photoluminescence (PL) properties of a GaInP epilayer with an ultrathin AlAs interfacial layer grown on Ge were investigated by time-resolved photoluminescence spectroscopy and temperature-dependent PL spectroscopy. A double-exponential PL decay with two time constants was observed, where the fast component is attributed to the emission from ordered GaInP while the slow component is related to localized states. Increased thickness of the AlAs interfacial layer resulted in an increased PL decay time due to the increased degree of order of the GaInP. Furthermore, the broad PL peak around 1.57 eV appearing in the GaInP epilayer after insertion of the AlAs layer might be attributed to phosphorus-vacancy-related deep levels.

**Keywords (separated by '-')**
GaInP epilayer - AlAs interfacial layer - time-resolved photoluminescence - decay time
Effects of Ultrathin AlAs Interfacial Layer on Photoluminescence Properties of GaInP Epilayer Grown on Ge

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The photoluminescence (PL) properties of a GaInP epilayer with an ultrathin AlAs interfacial layer grown on Ge were investigated by time-resolved photoluminescence spectroscopy and temperature-dependent PL spectroscopy. A double-exponential PL decay with two time constants was observed, where the fast component is attributed to the emission from ordered GaInP while the slow component is related to localized states. Increased thickness of the AlAs interfacial layer resulted in an increased PL decay time due to the increased degree of order of the GaInP. Furthermore, the broad PL peak around 1.57 eV appearing in the GaInP epilayer after insertion of the AlAs layer might be attributed to phosphorus-vacancy-related deep levels.

Key words: GaInP epilayer, AlAs interfacial layer, time-resolved photoluminescence, decay time

INTRODUCTION

The GaInP/Ge heterostructure is technologically important with potential applications in high-efficiency photovoltaic1 and light-emitting devices,2 and has been widely used in GaInP/(In)GaAs/Ge triple-junction solar cells.3,4 Recently, the efficiency of the GaInP/Ge triple-junction solar cell has reached 41.6% under 364 suns.5 Theoretical calculations for this combination of materials indicate that, to achieve maximum efficiency, the bandgap of the GaInP top cell should be as wide as possible, i.e., the GaInP should be completely disordered.6 In addition, in Ge-based multijunction solar cells, a Ge junction can be formed by diffusion of group V elements such as phosphorus (P) and arsenic (As) into the p-Ge substrate.7 Since P has a lower diffusion coefficient than As in Ge, Ga0.5In0.5P is often employed instead of GaAs as the nucleation layer grown on the p-type Ge substrate to form a relatively shallow Ge p−n junction.8 Therefore, high-quality growth of GaInP film on Ge substrate is crucial to the performance of solar cell devices with GaInP/Ge heterostructures. However, growth of III/V compound material on group IV substrate by metalorganic vapor-phase epitaxy (MOVPE) always suffers from the problem of antiphase domain (APD) defects, as well as interdiffusion of group III and V atoms with the Ge substrate, leading to degraded optical and electrical properties of the device.9–11 APD defects can be effectively suppressed through substrate miscut angle and high-temperature pregrowth surface treatment. Suppression of interdiffusion of group III and V atoms at the interface of the epilayer and Ge substrate has also been reported before, but mainly for interdiffusion between GaAs and Ge substrate. The methods used were, for example, growth of a low-temperature buffer layer or insertion of an interlayer with high bonding energy on the Ge substrate to act as a barrier layer between GaAs...
and Ge.\textsuperscript{12–15} Chia et al.\textsuperscript{14} demonstrated that the presence of an ultrathin AlAs interfacial layer at the GaAs/Ge interface dramatically blocked interdiffusion of Ge, Ga, and As atoms, due to the higher Al–As bonding energy. A deep broadband photoluminescence (PL) emission related to Ge complex centered around 1.4 eV, which might result from interdiffusion within the GaInP/Ge interface, has been reported.\textsuperscript{15} In our previous study,\textsuperscript{17} it was found that a superthin AlAs interfacial layer of 0.5 nm resulted in a decrease of the PL intensity arising from emission by \( \text{[Ge}_x\text{Ga}_{1-x}\text{In}_p\text{V}_{(x-x)}\text{]} \) complex.\textsuperscript{18} On the other hand, the thinner the \( p-n \) junction in the cell, the better the performance of the device.\textsuperscript{3} Such an AlAs interfacial layer at the GaInP/Ge interface can also suppress interdiffusion of P atoms to form a shallower \( p-n \) junction. In fact, in contrast to a GaAs epilayer on Ge, a GaInP epilayer on Ge suffers from an even more serious challenge, namely the problem of ordered and disordered structures, and more defects may occur.\textsuperscript{15,17}

To date, extensive research on the effect of an ultrathin AlAs interfacial layer on the PL and defect properties of a GaInP epilayer grown on germanium is scarce, but it might be critical for better control of the GaInP nucleation layer. In particular, the PL decay time is an important parameter to evaluate luminescence processes in semiconductors and related devices. It has been observed that ordered \( \text{Ga}_x\text{In}_{1-x}\text{P} \) exhibits a relatively long PL lifetime.\textsuperscript{16} In this work, we studied the PL properties of GaInP with different superthin AlAs interfacial layers by using time-resolved PL (TRPL) and temperature-dependent PL measurements. An increased AlAs thickness resulted in an increased PL decay time due to the increased degree of order. In addition, a broad PL peak at around 1.57 eV appearing in the GaInP epilayer after insertion of the AlAs layer is assigned to P-vacancy-related deep levels.

Epitaxially grown samples of undoped GaInP/AlAs/Ge, with AlAs interfacial layer thickness of 0.5 nm and 5 nm, were obtained using a horizontal low-pressure MOVPE system on Ga-doped \( p-Ga \) (100) substrates oriented with 9° misorientation toward (111). Trimethylgallium (TMGa) and trimethylindium (TMIn) were used as group III sources, \( \text{PH}_3 \) as group V source, and palladium-diffused \( \text{H}_2 \) as carrier gas. Nominally undoped GaInP epitaxial layers with thickness of about 228 nm were grown at 675°C, and the typical V/III ratio during growth was about 50. Before nucleation layer deposition, the Ge substrates were deoxidized at high temperature of 720°C and annealed in the \( \text{PH}_3 \) environment for several minutes. Transmission electron microscopy (TEM) measurements were carried out on the grown epilayer structures using an FEI F20 FEG operating at 200 kV. Continuous-wave (CW) PL was excited by the 532-nm line of a semiconductor laser and measured in the temperature range from 3 K to 200 K. Time-resolved PL spectra were measured using a synchroscan streak camera excited by a femtosecond pulse laser with excitation wavelength of 400 nm and pulse width of \( \sim 100 \) fs.

Figure 1 presents high-resolution cross-section TEM images of the undoped GaInP/AlAs/Ge structure for the samples with 0.5-nm and 5-nm AlAs; the inset presents corresponding transmission electron diffraction (TED) patterns in the (110) cross-section from GaInP. No dislocations or antiphase domains are observed in any epilayer, implying that their densities are very low. The structures show clear interfaces between the germanium substrate

![High-resolution TEM (110) cross-sectional images of undoped GaInP/AlAs/Ge structure for samples with 0.5-nm AlAs (a) and 5-nm AlAs (b). Insets show corresponding TED patterns.](Image)
and the AlAs and GaInP layers. As can be seen from Fig. 1a, the AlAs layer of the undoped GaInP/AlAs/Ge structure for the sample with 0.5-nm AlAs can be clearly seen in the TEM images, exhibiting well-aligned atomic planes between different layers. With the increased AlAs thickness, there exists a significant stress in the region of the AlAs layer, as shown in Fig. 1b. This means that the 5-nm-thick AlAs layer of the undoped GaInP/AlAs/Ge structure leads to stress accumulation due to lattice mismatch at the interface in the sandwich structure. The TED patterns in the (110) cross-section from GaInP presented in the insets of Fig. 1 can be employed to distinguish the degree of ordering in GaInP. For the undoped GaInP/AlAs/Ge structure with 0.5-nm AlAs, there are some 1/2 [111] superspots, while for the undoped GaInP/AlAs/Ge structure for the sample with 5-nm AlAs, a wider range of 1/2 (111) superspots can be clearly observed in the inset of Fig. 1b, indicating that the ordered matrix dominates in the GaInP epilayer of the undoped GaInP/AlAs/Ge structure for the sample with 5-nm AlAs.

Figure 2 presents the temperature-dependent PL spectra of the undoped GaInP/AlAs/Ge structure for the sample with 0.5-nm AlAs. With increasing temperature, the PL peak energy shows a blue-shift to the high energy side and then a red-shift to lower energy, as shown in the inset. This inverted "S-shape" of the PL energy temperature dependence is typically observed in material with incorporation of strong localized states. Very similar behavior was also observed for the undoped GaInP/AlAs/Ge structure with 5-nm AlAs. The photogenerated carriers in GaInP are mainly localized below the ordered band edge at low temperatures. Assisted by thermal energy, they can be thermalized into band states with increasing temperature. The localized states originate from the potential fluctuation induced by the compositional inhomogeneity of Ga and In in the partially ordered GaInP. The PL intensity competition process between localized states and free energy states in GaInP leads to the apparently S-shaped PL temperature dependence behavior. Figure 3a shows the TRPL spectra for the PL peak of the undoped GaInP/AlAs/Ge structure for the sample with 0.5-nm AlAs at low temperature (14 K) with the delay time changing from 125 ps to 275 ps. Near the band edge, only one PL peak at 1.87 eV can be observed, as shown in the inset of Fig. 3a. With increasing delay time, the PL peak shifts to the lower energy side. The variation of the PL peak energy as a function of the delay time can be explained by the interplay between radiative recombination and carrier transfer to free energy states. Very similar behavior was also observed for the undoped GaInP/AlAs/Ge structure with 5-nm AlAs, as shown in the inset of Fig. 3b.

Figure 4 shows the PL decay curves of the undoped GaInP/AlAs/Ge structure for the samples with 0.5-nm and 5-nm AlAs at low temperature of 14 K (a) and room temperature (b). The PL intensity in the decay curves is displayed on a logarithmic scale. The PL spectra for the undoped GaInP/AlAs/Ge structure with 0.5-nm and 5-nm AlAs measured at 14 K are shown in the inset of (a); the peak emission energy decreased from 1.874 eV to 1.868 eV when the AlAs layer thickness was increased from 0.5 nm to 5 nm. The PL spectra for the undoped GaInP/AlAs/Ge structure with 0.5-nm and 5-nm AlAs measured at room temperature are shown in the inset of (b); the peak emission energy decreased from 1.815 eV to 1.806 eV when the AlAs layer thickness was increased from 0.5 nm to 5 nm. Under pulsed laser excitation, only one PL peak was
Therefore, separation of this similar PL decay characteristic of 183 ps exist in the decay process, where 228 ps observed in GaInP on GaAs. Reduction of the material with ordering was also increased interfacial layer thickness. Bandgap of ordering of the GaInP epilayer increased with shown by the two materials indicate that the degree of order increases. The PL decay results to 14 K are shown in the inset to (a); the peak emission energy decreased from 1.874 eV to 1.868 eV with increased AlAs layer thickness from 0.5 nm to 5 nm. PL spectra of undoped GaInP/AlAs/Ge structure for samples with 0.5-nm AlAs (a) and 5-nm AlAs (b) measured at room temperature are shown in the inset to (b); the peak emission energy decreased from 1.815 eV to 1.806 eV with increased AlAs layer thickness from 0.5 nm to 5 nm.

undoped GaInP/AlAs/Ge structure with 5-nm AlAs. Similar to the PL decay behavior of GaInP grown on Ge with an AlAs interfacial layer at 14 K in our work, two exponential processes were observed in ordered GaInP grown on GaAs by other research groups, although the exact assignment of the sources of the two processes remained controversial.18,20-23 This similar PL decay characteristic of GaInP reflects an intrinsic property of GaInP material. According to the PL behavior related to both localized states and free energy states explained above, we believe that the source of the slow component at 14 K is related to the localized nature, whereas the source of the fast component is related to the free energy states in the ordered regions. It is important to note that both PL decay times, τ1 and τ2, increased when the thickness of the AlAs interfacial layer was increased from 0.5 nm to 5 nm. This behavior is attributed to the increased degree of ordering of GaInP for the increased AlAs thickness. According to the TED results mentioned above, the degree of ordering for the undoped GaInP/AlAs/Ge structure with 0.5-nm and 5-nm AlAs is different. It has been reported that the average size of ordered regions in GaInP increases with the degree of order.18 Therefore, separation of electrons and holes due to the effect of the piezoelectric field increases with increasing degree of order. So, the PL decay times become longer when the degree of order increases. The PL decay results indicate that a higher degree of order induced by the thicker AlAs interfacial layer plays an important role. It was found that the bandgap of the GaInP epilayer grown on Ge decreased when the interfacial layer thickness was increased from 0.5 nm to 5 nm. The different PL peak energies observed in GaInP on GaAs. The PL decay characteristic can be approximated by a double-exponential curve as \[ I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2), \] illustrating that two recombination mechanisms exist in the decay process, where \( I_1 \) and \( I_2 \) are the PL intensity of the two recombination mechanisms at \( t = 0 \), and \( \tau_1 \) and \( \tau_2 \) are the two PL decay times, i.e., fast and slow, respectively. At \( T = 14 \, K \), \( \tau_1 \) and \( \tau_2 \) are 37 ps and 555 ps for the undoped GaInP/AlAs/Ge structure with 0.5-nm AlAs, and 47 ps and 568 ps for the undoped GaInP/AlAs/Ge structure with 5-nm AlAs. At room temperature, a nearly single exponential decay curve is obtained, with decay time of 70 ps for the undoped GaInP/AlAs/Ge structure with 0.5-nm AlAs and 100 ps for the
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Consider the role in affecting the PL decay process, leading to longer decay times $\tau_1$ and $\tau_2$.

To obtain deeper insight into the effects of the ultrathin AlAs interfacial layer on the PL properties of GaInP on Ge, we carefully examined the temperature-dependent PL spectra in the low energy part. Figure 5 presents the PL spectra of the undoped GaInP/AlAs/Ge structure for samples with 0.5-nm and 5-nm AlAs at 100 K. Besides the PL peak at 1.36 eV arising from the emission of $[\text{Ge}^{(Ga,In)}\text{–V}^{(Ga,In)}]$ complex, an additional PL peak at 1.57 eV is observed for both samples, as shown in the enlarged part in the inset. The two PL peaks can be well fit by Gaussian fitting. The PL peak at around 1.36 eV could be observed for all the samples of GaInP grown on Ge in our previous work.$^{15,16}$ However, the PL peak at around 1.57 eV can only be observed for the samples with an ultrathin AlAs interfacial layer. Since the PL properties of Si-doped GaInP show a great difference compared with undoped GaInP, to confirm the correlation between the appearance of the 1.57 eV peak and the insertion of the AlAs interlayer, we also performed PL measurements on the Si-doped GaInP/AlAs/Ge structure for samples without AlAs and with 0.5-nm AlAs. The nominal doping density of silicon was $2 \times 10^{15}$ cm$^{-3}$. We obtained TED patterns in the (110) cross-section from Si-doped GaInP on Ge; the absence of 1/2 (111) superspots indicated that disordered matrix dominated in the Si-doped GaInP, as observed in our previous report.$^{15}$ Figure 6 presents the PL spectra of the two samples at 100 K. Without the AlAs interfacial layer, only one broad PL peak at 1.36 eV due to the emission of $[\text{Ge}^{(Ga,In)}\text{–V}^{(Ga,In)}]$ complex is observed in the low energy part. With incorporation of the AlAs interfacial layer, however, an unknown PL peak at about 1.57 eV appears. In addition, incorporation of the AlAs layer results in a reduction of the PL intensity of $[\text{Ge}^{(Ga,In)}\text{–V}^{(Ga,In)}]$ complex. In the high energy side of these spectra, three PL peaks appear near the band edge, being assigned to emissions from localized states (L), ordered GaInP (O), and disordered GaInP (D).$^{15}$

Deep levels in GaInP on Ge substrate are usually believed to be related to P vacancies and/or Ge-related complexes, as well as incompletely suppressed antiphase boundaries (APBs).$^{17}$ Considering the TEM results confirming that the GaInP epilayer with the ultrathin AlAs interfacial layer was free from APD defects, APBs should not be responsible for the emission at around 1.57 eV. In addition, the uncontrolled quaternary InGaAsP alloy is generally formed due to In carryover or As/P exchange when growing GaAs on GaInP. In our case, tens of GaInP epilayers with different thicknesses (from 100 nm to 700 nm) were grown on GaAs substrate. However, this kind of PL behavior was not observed. Therefore, we might exclude the possibility of InGaAsP. With incorporation of the AlAs interfacial layer, an increased degree of order of the GaInP epilayer was observed. On the basis of the combination of the step-terrace-reconstruction (STR) mode$^{24,25}$ with the dimer-induced stress model, a CuPt-B-type ordering of GaInP related to AlAs reconstruction with 2× periodicity is proposed to explain this effect. In this case, an increased P–P dimer together with the AlAs surface increases the driving force for formation of ordered GaInP. In contrast to GaInP on Ge, incorporation of the AlAs layer requires a high V/III ratio to achieve stable growth of GaInP. In addition, it has been reported that the CuPt-type ordered structure is not stable in the bulk.$^{27}$ Increased demands regarding the V/III ratio as well as the unstable nature of the ordered GaInP together might result in the possible lack of P–P dimers. Therefore, a P-vacancy-related emission can be observed. Furthermore, as shown in Fig. 5, in contrast to the undoped GaInP/AlAs/Ge...
structure for the sample with 0.5-nm AlAs, with increased degree of ordering of the GaInP epilayer, the PL intensity ratio of the 1.57 eV emission to the band-edge-related 1.87 eV emission increased in the undoped GaInP/AlAs/Ge structure for the sample with 5-nm AlAs, indicating that more P vacancies were generated with the increase of the degree of ordering of the GaInP epilayer. In addition, it has been reported based on the electrical characterization method that a P-vacancy-related deep level is located at 0.28 ± 0.02 eV below $E_C$ in the Ga$_{0.51}$In$_{0.49}$P/GaAs heterojunction grown by molecular beam epitaxy. For the undoped GaInP/GaAs/Ge structure for the samples with 0.5-nm AlAs and 5-nm AlAs, the energy separation between the band-edge-related emission (1.87 eV) and the 1.57 eV emission is 0.3 eV, falling within the range of emission energy difference between P-vacancy-related deep level and $E_C$. Since the 1.57 eV emission is also observed in Si-doped GaInP with a highly disordered material, as shown in Fig. 6, we tentatively attribute the 1.57 eV emission to P-vacancy-related PL.

CONCLUSIONS

We investigated the PL properties of a GaInP epilayer with an ultrathin AlAs interfacial layer grown on Ge. Increased thickness of the AlAs interfacial layer resulted in an increased PL decay time due to an increased degree of ordering of the GaInP. Furthermore, a broad PL peak appearing at around 1.57 eV in the GaInP epilayer after insertion of the AlAs layer might be attributed to phosphorus-vacancy-related deep levels. However, for multijunction solar cell applications, one cannot benefit from the more ordered structure of GaInP due to the AlAs layer, although the AlAs layer can effectively reduce the PL arising from the emission of [Ge$_{Ga,In}$-V$_{Ga,In}$] complex. The disadvantage of the effect of the AlAs layer on the material properties must be overcome before its application in future multijunction fabrication.

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