GaP layers grown on GaN with and without buffer layers*

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The growth of GaP layer on GaN with and without buffer layers by metal-organic chemical vapour deposition (MOCVD) has been studied. Results indicate that the GaP low temperature buffer layer can provide a high density of nucleation sites for high temperature (HT) GaP growth. These sites can promote the two-dimensional (2D) growth of HT GaP and reduce the surface roughness. A GaP single crystal layer grown at 680 °C is obtained using a 40-nm thick GaP buffer layer. The full-width at half-maximum (FWHM) of the (111) plane of GaP layer, measured by DCXRD, is 560 arcsec. The GaP layer grown on GaN without low temperature GaP buffer layer shows a rougher surface. However, the FWHM of the (111) plane is 408 arcsec, which is the indication of better crystal quality for the GaP layer grown on GaN without a low temperature buffer layer. Because it provides less nucleation sites grown at high growth temperature, the three-dimensional (3D) growth is prolonged. The crystalline quality of GaP is lightly improved when the surface of GaN substrate is pretreated by PH_3, while it turned to be polycrystalline when the substrate is pretreated by TEGa.

Keywords: metal-organic chemical vapour deposition, semiconductors, gallium phosphide, gallium nitride, x-ray diffraction

PACC: 7280E, 8115H

1. Introduction

III-nitrides and their alloys have attracted much attention for applications in electronic and optoelectronic devices.[1−3] However, despite the remarkable progress in device performance, there still remain many problems that need to be solved. One of the difficulties lies in the low hole concentration of p-type layer due to the low Mg ionization percentage, which results in a highly resistive p-type GaN layer and a large metal/p-type GaN contact resistance.[4−6] It is important to obtain a suitable p-type layer with a high hole concentration to improve the performance of GaN based devices. In contrast, InGaAsP compounds have relatively good p-type properties. The carrier concentration of p-GaP could easily reach 5×10^{18} cm^{-3}.[7,8] In recent years, high performance InGaAsP compound optoelectronic devices have been successfully fabricated.[8−11] If good quality InGaAsP compounds can be grown on III-nitride, the performance of GaN based devices could possibly be improved by utilizing the good p-type properties of InGaAsP compounds, such as GaP. More importantly, it provides the possibility of the integration of InAlGaN and InGaAsP materials to produce new devices, such as infrared/ultraviolet detector, solar cell, and so on.

The GaP (111) plane has the same symmetry as the *c*-plane of wurtzite GaN. However, it is probably difficult to grow high-quality GaP films on GaN because of the large lattice mismatch between GaP and GaN (17.2%). In recent years, researches on this topic only studied GaN layer grown on GaP layer.[12,13] In the present paper, we investigate the growth of GaP layers on GaN by MOCVD. The effects of the buffer layer and the pretreatment on the growth of GaP are investigated. The GaP single crystal layers are obtained.

2. Experiment

The high-resistance lightly Mg-doped GaN layers on (0001) *c*-plane sapphire wafers were grown in

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an MOCVD system with the Thomas Swan closely spaced showerhead reactor. The GaN films were placed in an EMCORE GS/3200 LP-MOCVD system to grow the GaP layers. The source materials were TEGa and PH_3, respectively. Hydrogen (H_2) was used as carrier gas. Prior to the GaP growth, GaN layer was heated under the hydrogen ambient at 700 °C for 5 min in order to remove contaminants. During GaP layer growing, the mole flow rate of TEGa was fixed at 6.9×10^{-5} mol/min and the V/III ratio was 100. The growth pressure was 8.0×10^{3} Pa. Other parameters, such as buffer layer, and pretreatment, were changed for analysis and comparison.

Structural properties of the GaP layers were investigated by double crystal x-ray diffraction (DCXRD). The electrical properties were measured by Van der Pauw Hall method and universal meter at room temperature. The surface morphology was observed with atomic force microscopy (AFM). The layer thickness and the growth rate were confirmed using cross-sectional scanning electron microscope (cross-sectional SEM).

3. Results and discussion

Figure 1 shows AFM images of the two GaP samples, the scanning area of each sample was 5 μm×5 μm. Sample A was directly grown on GaN without low temperature GaP buffer layer. The growth temperature of sample A was 680 °C. During sample B growing, a 40-nm thick GaP buffer layer was deposited at 400 °C. Then, the temperature was increased and maintained at 680 °C or 6 min. Finally, high temperature (HT) GaP layers were grown at 680 °C. As shown in Fig. 1, the surface morphologies of the two samples are different. Some triangular shape grains appear on the surface of sample A (without buffer layer), which are shown by arrows. This is typical character of (111) plane of GaP, and it indicates that the GaP layers are grown along the (111) direction. However, a hillock-like feature appears on the surface of sample B (with buffer layer). The root mean square (RMS) values of samples A and B are obtained by AFM to be 96.6 nm and 32.8 nm, respectively. The RMS value of sample B is dramatically lower than that of sample A, which is coincident with the difference in surface morphology between the two samples. Different from sample A, sample B presents a hillock-like feature. It means that the coalescence of triangular shape grains happens and the surface of GaP becomes flat gradually. Correspondingly, a flater surface is observed.

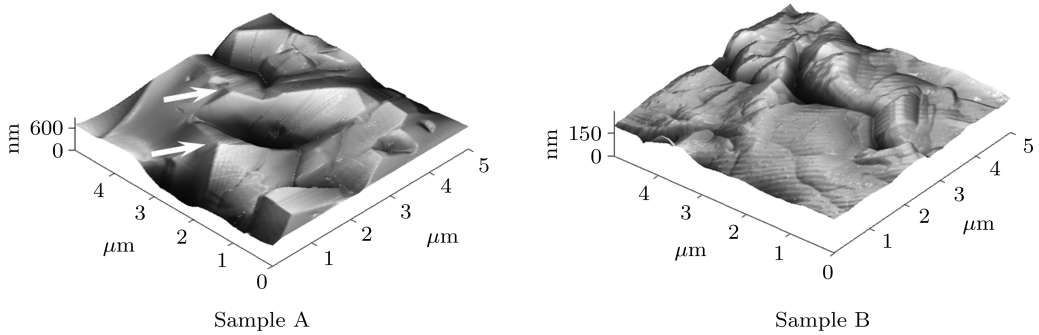


Fig. 1. 5×5 μm^2 3D AFM images of GaP films grown on GaN without (sample A) and with (sample B) low temperature buffer layers.

Figure 2 shows DCXRD ω–2θ rocking curves of these two samples. It can be seen that there are seven peaks in each sample. The peaks of (0002) and (0004) planes are attributed to the GaN layer. The peaks near 22° and 46° are produced by the sapphire substrate. The peaks of (111), (222) and (333) planes belong to the GaP layer. The two GaP layers have only the symmetrical peaks of (111), (222), and (333) planes, indicating that both GaP samples are of single crystal structure. An omega-scan was used to obtain the line width of (111) plane of GaP layer. Figure 3 shows the DCXRD ω rocking curves for (111) planes of GaP layers of the two samples. The values of full-width at half-maximum (FWHM) of (111) planes for

samples A and B are 408 arcsec and 560 arcsec, respectively. The FWHM value of sample A is obviously narrower than that of sample B, which means that the GaP layer directly grown on GaN has a better crystal quality than that with low temperature buffer layer. This indicates that GaP layer can be directly grown on GaN, even there is a large lattice mismatch between GaP and GaN (17.2%).

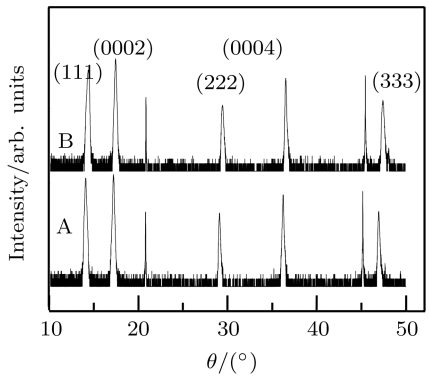


Fig. 2. Double crystal x-ray diffraction ω–2θ rocking curves of GaP films grown on GaN without and with low temperature buffer layers

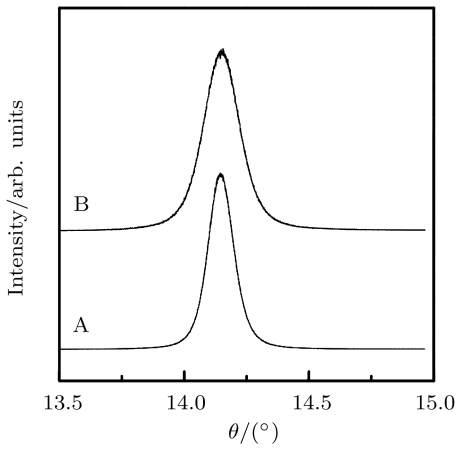
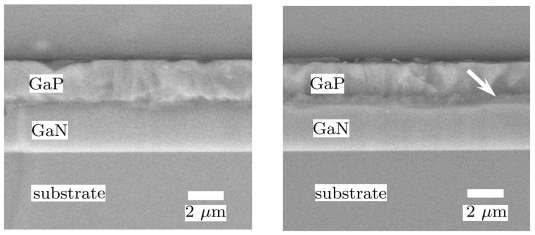


Fig. 3. Double crystal x-ray diffraction ω rocking curves of GaP films grown on GaN without and with low temperature buffer layers.

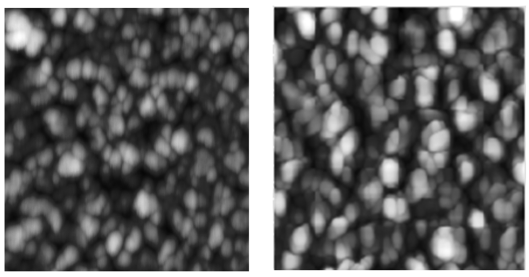
Figure 4 shows cross-sectional SEM images of the two samples. The growth rates of both samples are estimated by SEM to be 2.0 μm/h. As shown in Fig. 4, there are some differences between the two samples. For GaP grown on low temperature GaP buffer layer (sample B), there seems to be an interlayer between GaN and GaP, which is shown by arrow. The thickness of the interlayer is about 0.5 μm. However, this phenomenon is not observed in sample A, which was directly grown on GaN.



Sample A Sample B

Fig. 4. Cross-sectional SEM images of GaP films grown on GaN without and with low temperature buffer layers.

In order to investigate the influence of the buffer layer, we grew a 40-nm thick GaP buffer layer on GaN (sample C) using the same parameters as those of the low temperature GaP buffer layer in sample B. For comparison, another 40-nm thick HT GaP layer (sample D) was directly grown on GaN at 680 °C using the same parameters as those of sample A. Figure 5 shows the AFM images of these two samples. The scanning area of each sample was 1×1 μm^2. It can be seen that the surface morphologies of the two samples are different. The grain density of sample C (low temperature buffer layer) is obviously higher than that of sample D (HT GaP layer). And the grain size of sample C (∼30 nm) is obviously smaller than that of sample D (∼60 nm). The RSM values from AFM for samples C and D are 1.8 nm and 8.3 nm respectively, indicating that three-dimensional (3D) growth is obvious at high growth temperature. These phenomena are reasonable because of the large lattice mismatch between GaP and GaN. The lager lattice mismatch between GaP and GaN would induce a 3D growth mode of GaP on GaN, just as GaN layer is grown on Al_2O_3 substrate.[14,15] On the other hand, the transfer velocity of atoms on the surface would increase with growth temperature increasing. So, the triangular shape grain appears and the size increases with temperature increasing.



(a) Grown at 400 °C (b) Grown at 700 °C

Fig. 5. 1×1 μm^2 AFM images of a 40-nm thick GaP buffer layer grown at 400 °C (sample C) and a 40-nm thick GaP layer grown at 700 °C (sample D).

Generally, large lattice mismatch between epilayer and substrate would induce a 3D island growth. The epilayer starts to grow in an island-like growth mode, i.e., grains form at the nucleation sites which grow both in the lateral direction and in the normal direction. Finally, the coalescence of grains happens and a 2D growth mode is established. The morphologies of two 40-nm thick GaP layers in Fig. 5 and the morphologies of samples A and B suggest that the growth mechanisms of GaP on GaN with and without low temperature buffer layers are different. For GaP grown using a low temperature buffer layer (sample B), the buffer layer provides a high density of small size nucleation sites for high temperature GaP growth (see the morphology of sample C). And the buffer layer has a flater surface due to the low growth temperature. These small smooth nucleation sites can effectively promote the 2D growth mode, and a smooth surface could be more easily obtained. For HT GaP directly grown on GaN without low temperature buffer layer (sample A), the grain size initially is obviously larger and rougher (see the morphology of sample D). These large size rough grains would prolong the 3D growth, which results in a rougher surface and obviously triangular shape grains. On the other hand, the crystal quality of GaP layer is also influenced by the island size because many defects are formed in the process of island coalescence. The larger island size would reduce the interface region, which results in a reduction of the defect density. Thus, the crystal quality of GaP layer grown with low temperature buffer layer becomes worse because the GaP island sizes are small. However, the GaP layer grown without low temperature buffer has a better crystal quality, although it has rougher surface.

For studying the influence of pretreatment on the properties of GaP layer, we grew two GaP samples. Figure 6 shows the DCXRD ω–2θ rocking curves of these two samples. During growing sample E, the surface of GaN substrate was pretreated by PH_3 with a flow ratio of 5.5×10^{-4} mol/min at 700 °C for 60 s prior to the GaP layer growth. The surface of GaN substrate of sample F was pretreated by TEGa with a flow ratio of 6.9×10^{-5} mol/min at 700 °C for 30 s prior to the GaP growth. Sample E presents only the peaks of (111), (222) and (333) planes, which means that the GaP layer is of single crystal. The FWHM values of (111) plane for sample C is only 392 arcsec, which means that the crystal quality of GaP layer can be slightly improved when the surface of GaN substrate was pretreated by PH_3. However, when the surface of GaN substrate was pretreated by TEGa, the peak of (220) plane of GaP appears. It indicates that the GaP layer is polycrystalline. We think that an ultra-thin GaNP layer is probably formed when the GaN is pretreated by PH_3. It would reduce the lattice mismatch between GaP and GaN and improve the quality of GaP layer. However, the pretreatment by TEGa would result in Ga atoms depositing on GaN. The quality of GaP becomes worse and polycrystalline since GaP layer is grown on Ga grains in some regions.

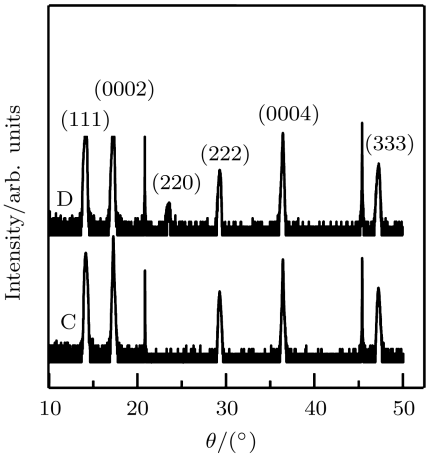


Fig. 6. Double crystal x-ray diffraction rocking curves of GaP films grown on GaN with PH_3 (sample E) or TEGa (sample F) pretreatment.

4. Conclusion

The GaP low temperature buffer layer can provide a high density nucleation sites for high temperature (HT) GaP growth, which can promote the 2D growth of HT GaP. A GaP single crystal layer, whose FWHM of the (111) plane was measured by DCXRD to be 560 arcsec, is grown at 680 °C using a 40-nm thick GaP buffer layer. The GaP layer grown on GaN without low temperature GaP buffer layer shows a rougher surface. However, The FWHM of the (111) plane is 408 arcsec. In our experiment condition, the GaP layer grown on GaN without a low temperature buffer layer has a better crystal quality. The crystal quality of GaP is slightly improved when the surface of GaN substrate is pretreated by PH_3. However, the GaP layer turns to be polycrystalline when the surface of GaN substrate is pretreated by TEGa.

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