Single-phase growth studies of GaP on Si by solid-source molecular beam epitaxy

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GaP/Si heterostructures were grown under different growth conditions by molecular beam epitaxy in order to obtain single-phase GaP on Si. The growth results were examined by reflective high-energy electron diffraction, anisotropic etching, atomic force microscopy, and x-ray diffraction. The results showed that high quality, single-phase GaP was grown on Si at a high growth temperature, about 500 °C, with a low P/Ga flux ratio of 2.5×, while at a lower temperature, a second phase with a 90° in-plane rotation was grown. © *2004 American Vacuum Society.*
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I. INTRODUCTION

Remote gas detection and military airborne countermeasures need convenient, midinfrared laser sources with narrow wavelength linewidth, high output power, and wide wavelength tunability. There are several potential approaches that can satisfy these needs, including direct-emitting semiconductor lasers and nonlinear optical devices.[1,2] Nonlinear optics has become a very attractive approach due to its flexibility in wavelength tuning, possibilities for high or low power, and continuous-wave or pulsed operation, and the possibility for room temperature operation. This approach has been demonstrated in birefringent phase-matched materials and quasiphase-matched materials such as periodically poled $LiNbO_3$, orientation-patterned GaAs.[3,4] The zinc-blende semiconductors, including GaAs, GaP, and ZnSe, have desirable properties for nonlinear optical frequency mixing. Among these, GaP has the most attractive properties. In addition to its high nonlinear coefficient (45 pm/V),[5] GaP has very high thermal conductivity (1.1 W/cm K), which is several orders of magnitude higher compared to other nonlinear crystals. This large thermal conductivity allows efficient heat extraction so that high pump powers and high output powers can be achieved. It has a very low absorption coefficient, particularly in the visible and near-infrared region. This minimizes two-photon absorption, which is a by-product of nonlinear difference frequency generation process. It also has a very broad transparency range (0.6–11 μm), which enables pumping with a visible wavelength laser source. These properties have made GaP an attractive nonlinear optical material.

Unfortunately, the isotropic nature of the zinc-blende structures precludes birefringent phasematching in GaAs or GaP. Quasiphase matching (QPM) eliminates this problem by spatial modulation of the nonlinear optical coefficient. Various techniques have been developed to achieve QPM in these materials, including stacking wafers, wafer bonding, and orientation patterned growth. Orientation patterned structures fabricated by an all-epitaxial process is a highly promising approach that has recently been used to demonstrate optical frequency mixing in GaAs.[6–8] The orientation-patterned GaAs or GaP (OP–GaAs or OP–GaP) structure is shown in Fig. 1(a). It has periodic domains, where the two adjacent domains have a 90° rotation about the (001) axis. Since this rotation reverses the sign of the nonlinear coefficient, the nonlinear coefficient is spatially modulated. Figure 1(b) shows the atomic arrangement of a GaP/Si/GaP heterostructure viewed along the [110] direction, where the stacking sequence of GaP on Si is different from the GaP below Si due to the 90° rotation. After photolithography and chemical etching, the surface of different phases is alternately exposed, and the subsequent regrowth will form the QPM structure shown in Fig. 1(a). Si is used to alter the stacking sequence of the Ga and P atoms due to the purely covalent bonding for Si. To fabricate the OP–GaP structure, at least one phase of GaP must be grown on Si, thus a GaP substrate with a 90° rotation can be chosen. If both phases of GaP can be grown on Si by controlling the growth parameters, then Si substrates can be used rather than more expensive GaP substrates.

The essential element of the growth process is to control the phase of GaP grown on Si. However, polar-on-nonpolar heteroepitaxy has its unique problems, namely, the difference in lattice symmetry between the III–V and group IV materials creates antiphase domains bounded by the antiphase boundaries in the III–V epilayer.[9] The growth parameters and growth methods of GaP on Si have been investigated by Wright, Bi, and other researchers using molecular beam epitaxy (MBE),[10–13] and high quality GaP has been reported under various growth conditions. However, compared with GaAs growth on Ge, insufficient work has been done to identify the GaP phase or orientation. The aim of this article is to report our results of single-phase GaP growth on Si by MBE by controlling growth temperature and V/III flux ratio. Reflection high-energy electron diffraction (RHEED) is used as the *in situ* and first evidence for phase identification. Anisotropic etching *ex situ* reveals the sidewall profile that identifies the phase orientation. X-ray diffraction (XRD) and atomic force microscopy (AFM) are carried out to characterize the crystalline quality and surface morphology.

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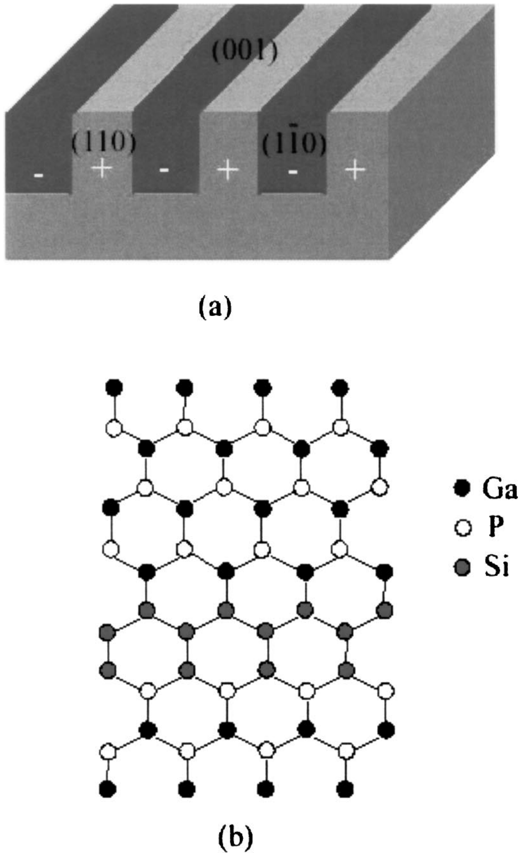


FIG. 1. Orientation patterned GaP. (a) The schematic of orientation patterned GaP. (b) GaP/Si/GaP heterostructures.

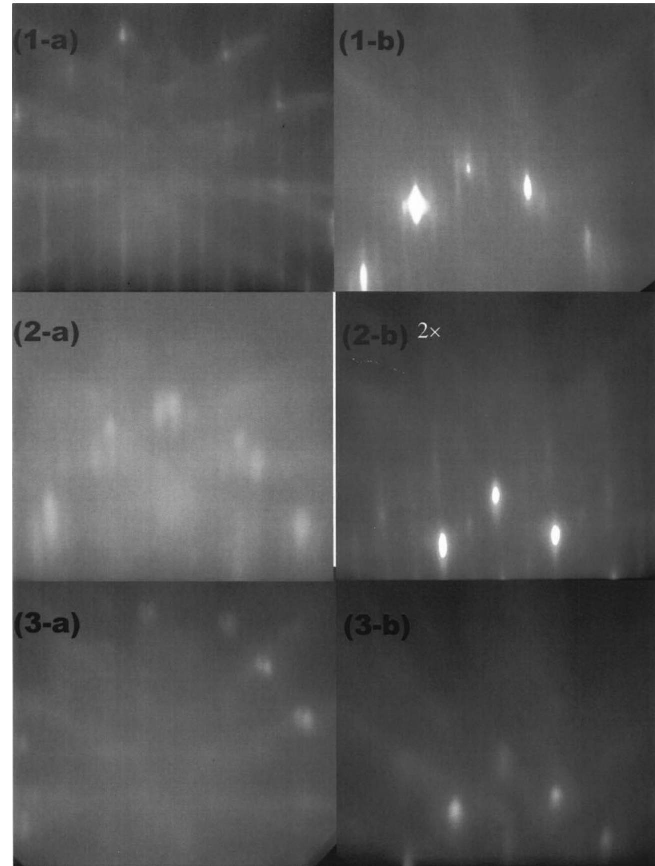


FIG. 2. RHEED pattern of GaP grown on Si under different growth conditions: (1) $T_s = 575\,°C$; (2) $T_s = 350\,°C$, two-step growth; (3) $T_s = 350\,°C$, one-step growth. (a) Perpendicular to the surface step and (b) parallel to the surface step.

II. EXPERIMENT

GaP films were grown in a Varian GEN II MBE system. P_2 flux was provided by a GaP decomposition cell with a P_2 partial pressure as high as 99%.[14] Phosphorous doped Si substrates with 4° off (001) towards the ⟨110⟩ direction orientation were used for MBE growth. From our earlier GaAs on Ge work, we found 4° off substrates provide a good offset angle for single phase growth, which is the basis for our choice of 4° offset Si substrate for GaP growth. The Si substrates were cleaned using a modified Radio Corporation of America clean methods [10 min in $H_2SO_4:H_2O_2$ (4:1) at 90 °C; 10 min in H_2O:HCl:H_2O_2 (5:1:1) at 70 °C; 15 s in HF (50:1) at room temperature; spin dry]. A final HF de-ionized water (1:100) solution dip for 10 s was performed right before loading into the MBE prechamber with a pressure about 1×10^{-8} Torr. After baking, the wafers were transferred to MBE growth chamber with a pressure below 2.0×10^{-10} Torr. A 30 min oxide desorption was performed at 850 °C before growth initiated. A strong 2×1 RHEED pattern mixed with a weak 1×2 RHEED pattern was observed before growth. The growth was started with a phosphorus prelayer by exposing the substrate to phosphorus for 3 min at the growth temperature before any Ga deposition. The GaP growth rate was kept at 0.2 μm/h during all the growth. The growth temperature was monitored by a thermal couple adjacent to the backside of substrates.

For most of the growth, a single-step growth process was used; that is, the nucleation temperature and the continuing growth temperature are the same. Two-step growth process was performed when a low nucleation temperature was used. In the two-step growth, a thin nucleation layer was grown at a low temperature (about 350 °C), and then a thicker film was deposited at a high temperature (around 700 °C). A series of growths were carried out by varying the nucleation temperature between 350 and 550 °C when the single-step growth was used. The flux ratio of P/Ga was selected from 2–10×. Growth results showed that a flux ratio lower then 2× results in Ga condensation on the surface, and no crystalline GaP was grown.

III. RESULTS AND DISCUSSION

A. RHEED observation

GaP exhibits a 2×4 GaP RHEED pattern under both low and high temperature. The quality of the film and the film orientation can be monitored using the RHEED pattern because it is known that the 4× is observed when electron beam is along [1 −1 0].[15] As demonstrated in Fig. 2, due to the offset angle of the substrate, the Kikuchi lines will oscillate around the horizon when the substrate is rotating. The lines intersect either above or below the horizon when the

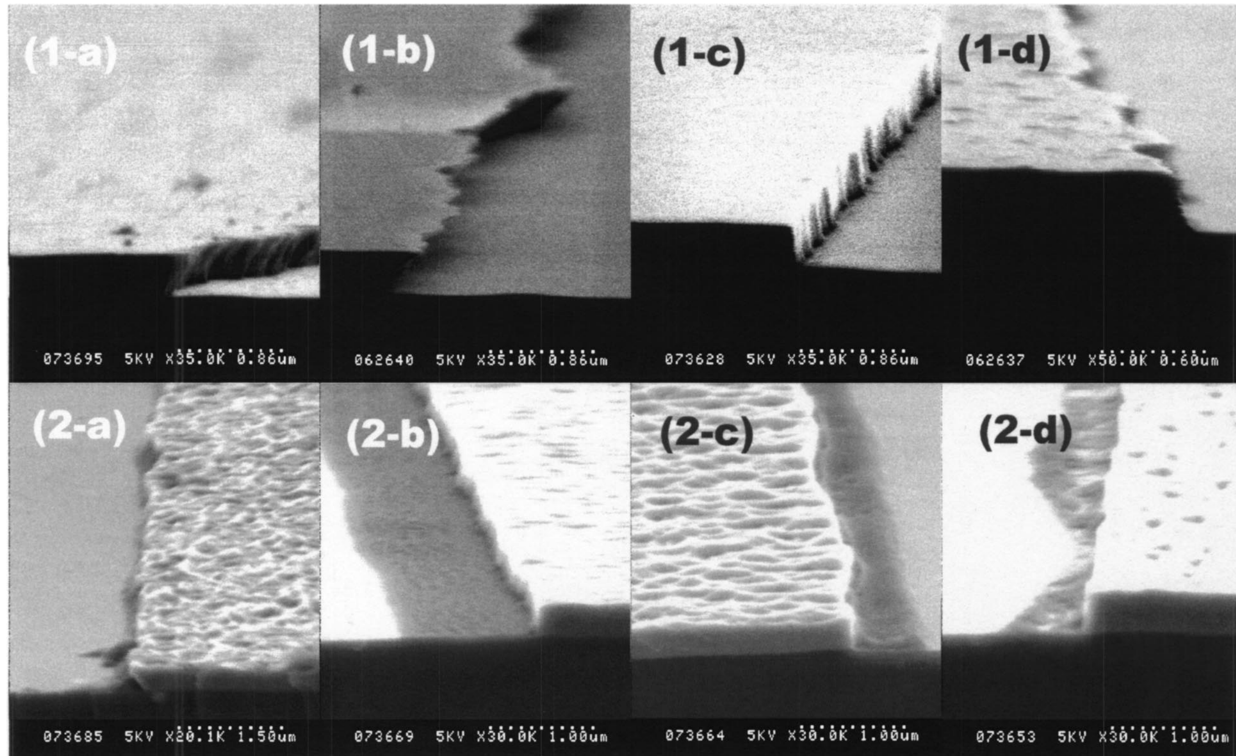


FIG. 3. SEM of the sidewall profiles after anisotropic etching. Flux ratio: (1) P/Ga=2.5×; (2) P/Ga=8×. Growth temperature: (a) 550; (b) 500; (c) 450; and (d) 400 °C.

electron beam is along the 4° misoriented direction (perpendicular to the steps), and intersect on horizon when electron beam is perpendicular to the misoriented direction (parallel to the steps). Figure 2 shows a 2×4 RHEED pattern at high growth temperature $T_s = 575\,°C$ with a low P/Ga flux ratio =2.5×. The 2× reconstruction is observed when electron beam is along the misoriented direction, and the 4× reconstruction is seen after the substrate is rotated by 90°. The streaky characteristic of the RHEED pattern indicates that a smooth GaP surface was achieved under this growth condition. As the growth temperature is decreased to $T_s = 350\,°C$, as shown in Fig. 2, a 4×2 reconstruction is observed for the two-step growth. This difference between RHEED patterns indicates that different phases are achieved at different temperatures.

The RHEED pattern of the low temperature growth by the single-step growth is also shown in Fig. 2. Under this growth condition, the RHEED pattern is spotty and reconstruction can hardly be observed, thus the single-step growth under low growth temperature results in a rough surface and low film quality. In comparison, the two-step growth has a smoother surface, though it is still rougher than the high-temperature phase as indicated by the RHEED pattern.

B. Anisotropic etching result

In addition to examining the RHEED pattern, we further confirmed that different phases had been grown by performing anisotropic etching of the GaP film. Scanning electron microscopy (SEM) was used to observe the sidewall profile after etching. A solution of HBr:H_2O_2:H_2O=1:1:3 was used due to its etching rate difference of (111)A and (111)B planes.[16] The etching time was about 50 s for 4000 Å GaP on Si. Because the (111)A plane etches slowly, the sidewalls of the etching profile will be either obtuse or acute for the different GaP phases. Figure 3 shows SEM pictures of the sidewall profiles under different growth temperatures and P/Ga flux ratios. At a low flux ratio of 2.5×, the sidewall profiles are acute for temperatures higher than 500 °C, and obtuse at lower temperatures of 400 °C. The difference in the sidewall profile proves the phases are different under different growth temperature. The acute sidewall indicates that the phase with 4° off (100) towards (111)A plane grows at high temperature, and the obtuse sidewall means 4° off (100) towards (111)B plane is achieved at low growth temperature. In addition, we see that the surface of high temperature growth is smoother than that of the low temperature growth. At 450 °C temperature and same flux ratio of 2.5×, the sidewall is vertical, which indicates that mixed phases have been grown. Thus, the threshold temperature for the phase selection is about 450 °C when the flux ratio is equal to 2.5×.

As shown in Fig. 3, when the flux ratio is increased to 8×, an acute sidewall is still observed for growth at 550 °C. However, all the sidewalls are vertical for all temperatures <500 °C. The etching profiles indicate that a high flux ratio increases the threshold temperature for phase selection. It is still uncertain why the low temperature phase disappears under high flux ratio, but it is possible, that the large roughness changes the surface properties controlling phase selection.

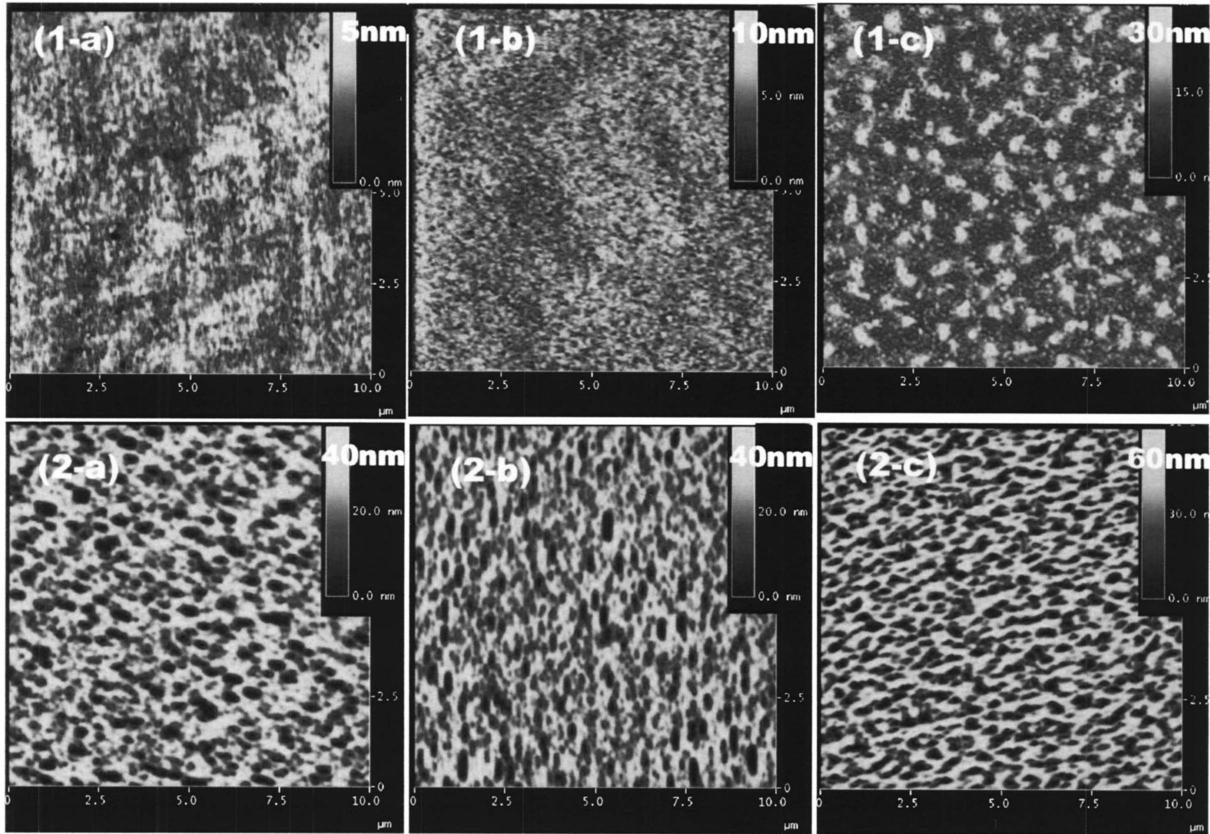


FIG. 4. AFM image of as-grown GaP film on Si. Flux ratio: (1) P/Ga=2.5×; (2) P/Ga=8×. Growth temperature: (a) 500; (b) 450; and (c) 400 °C.

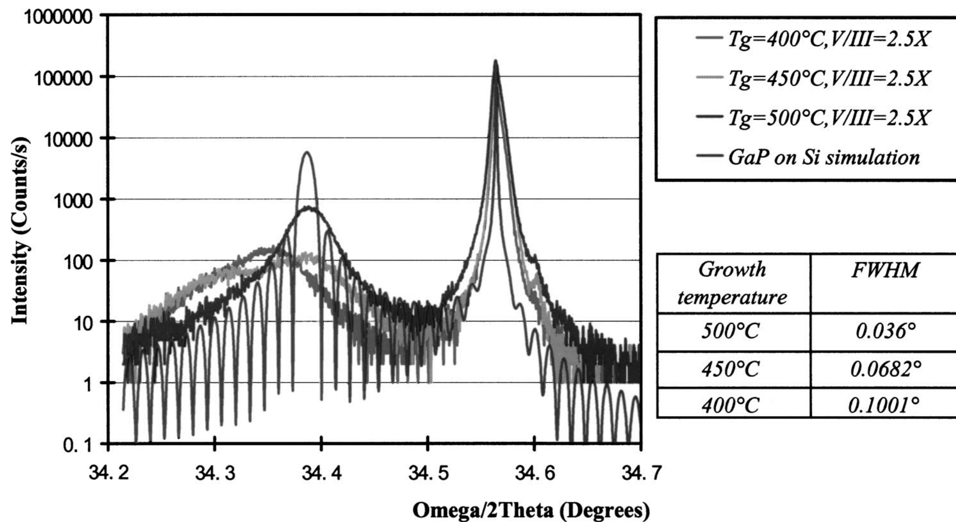
The phenomenon of temperature-dependence phase selection has also been observed in GaAs growth on Ge. Li *et al.*[17] explained this phenomenon through competition mechanisms of terrace-dominated versus step-dominated nucleation. Nucleation occurs on both steps and terraces simultaneously, but with competing domains. At high temperatures, the Ga atoms have enough time to migrate to the step location, where it has the lowest energy states, thus resulting in single-phase materials that correspond to the step nuclei. At low temperatures, the terrace nuclei dominate and this results in a phase opposed to the high temperature phase. At the temperature between them, both terrace nuclei and step nuclei grow up, thus mixed phases are formed. However, according to their theory, the GaAs phase with 4° off (100) towards (111)B plane will grow on Ge at a high temperature, while the phase with 4° off (100) towards (111)A plane will grow at a low temperature, which is in direct contrast with our observation of GaP growth on Si. The reason for this contradiction may be explained by the use of high H_2 concentration in metalorganic chemical vapor deposition growth, as opposed to MBE growth, which may change the stable phase in a different process, but further investigation is needed to fully understand this phenomenon.

C. AFM results

AFM gives a quantitative characterization of the surface roughness. Figure 4 shows an AFM image of the films grown under different growth conditions. At a low flux ratio of 2.5×, high temperature (500 °C) growth results in a very smooth surface, and the peak-to-valley distance is below 5 nm. This smooth surface corresponds to the single phase grown at 500 °C as seen in Fig. 3. The surface roughness increases with decreasing temperature, and the peak-to-valley distance is 10 nm at 450 °C vs 30 nm at 400 °C. Low temperature growth results in very rough surfaces even at a low flux ratio. At the high flux ratio 8×, the surface is rough even at a high growth temperature. All the growths have a roughness of about 40 nm. Thus, based on the earlier observation, and that of phase selection and surface quality, a low flux ratio is best for GaP growth on Si. However, if the flux ratio decreases below 2×, the P flux is not sufficient to maintain P-stable surface and Ga droplets form. The best flux ratio is ~2.5× and this conclusion is consistent with Wright's results.[16]

D. XRD result

XRD was carried out using a Philips X'Pert PRO x-ray diffraction system with an angular resolution up to 0.0001°. Figure 5 shows the XRD measurement of the samples that have been grown at various temperatures with a flux ratio of 2.5×. All the films have a thickness of 4000 Å. Comparing their peak position and peak width, the sample grown at 500 °C shows the best crystalline quality. The GaP (004) peak position matches the simulated results, and the peak



Growth temperature	FWHM
500°C	0.036°
450°C	0.0682°
400°C	0.1001°

FIG. 5. XRD results of the as-grown GaP film on Si.

width is very narrow with full width at half maximum (FWHM) = 0.036°. This means a uniform and strain-free film has been grown under this condition. This result is better than that of previously reported work.[11] With deceasing growth temperature, the GaP (004) peak shifts to a smaller angle and the peak intensity decreases. At the same time, the GaP peak is severely broadened. These changes indicate that the film grown at low temperatures is strained and the strain in the film is not uniform. The peak of the sample grown at 450 °C is the broadest and the two subpeaks can be resolved. This temperature was identified as the threshold temperature for determining the phases, thus the competition between different phases at the boundary degrades the film quality.

IV. CONCLUSION

We have shown that single phase GaP can be grown on Si. The growth temperature has been identified as the most important parameter that determines which phase can be grown. At high temperature and low flux ratio, a single phase with 4° misorientation off (001) towards the (111)A plane is grown while at low temperature, the other phase with 4° off (001) towards the (111)B plane is achieved. The threshold temperature range is affected by the flux ratio where a high flux ratio increases the threshold temperature. For a flux ratio 2.5×, the threshold temperature is ~450 °C. A high flux ratio also causes severe roughening of the GaP film, thus the flux ratio should be as low as possible to maintain P-stable growth. The best range is 2–3×. At this flux ratio and at 500 °C, high quality single phase GaP has been grown. The surface peak-to-valley distance given by AFM is 5 nm and the XRD gives FWHM = 0.036° for the GaP (004) peak. Although the low temperature phase has poor quality, a two-step growth can be used to improve the surface quality. These results are very encouraging and provide a foundation for the development of the OP–GaP based nonlinear devices.

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