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<th>Metalorganic chemical vapor deposition-regrown Ga-rich InGaP films on SiGe virtual substrates for Si-based III-V optoelectronic device applications</th>
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<td><strong>Author(s)</strong></td>
<td>Kim, TaeWan; Wang, Bing; Wang, Cong; Kohen, David A.; Hwang, Jeong Woo; Shin, Jae Cheol; Kang, Sang-Woo; Michel, Jürgen</td>
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I. INTRODUCTION

Several approaches have been pursued to achieve high quality semiconductors with a bandgap of 2.0–2.5 eV, which are used in multijunction solar cells and green (or yellow-green) light emitting diodes (LED). There are two possible material architectures for growing these materials. The first method includes depositing group III-nitride (III-N) materials (i.e., InGaN) on Si, GaN, or sapphire substrates. In spite of technical progress in III-N materials, the high cost and limited area of growth remain a challenge in producing In-rich InGaN for emission in the green wavelength range. The second method employs III-(As)P, such as InGaP, AlInP, and GaAsP, via compositionally graded Si_xGe_{1-x}, GaAs_yP_{1-y}, or In_{x}Ga_{1-x}As metamorphic buffer layers (MBL) on GaAs, GaP, or Si substrates. Both methods have the potential to achieve optoelectronic devices targeting the green wavelength range. There are a few prior achievements of yellow-green LEDs using lattice-mismatched relaxed In_{0.3}Ga_{0.7}P (Refs. 1–3) and Al_{0.4}In_{0.6}P (Ref. 4) on GaP and GaAs substrates employing compositionally graded GaAs_{y}P_{1-y} and In_{x}Ga_{1-x}As MBLs. No systematic studies have been reported on bulk Ga-rich InGaP films grown directly on Si substrate employing Si_{x}Ge_{1-x} compositionally graded buffer layers.
(SixGe1-x virtual substrates). Although other research groups have demonstrated III-V solar cells on Si substrates employing compositionally graded SixGe1-x MBL,5,6 it is challenging to produce high quality III-V alloys on a SixGe1-x virtual substrate due to point defects, threading dislocations, and stacking faults.8

In this study, we report MOCVD-grown films of Ga-rich InGaP on Si substrates employing SixGe1-x metamorphic buffer layers, targeting emission in the orange-yellow wavelength range. The structural and optical properties of Ga-rich InGaP films were characterized to determine the amount of In, Ga, and P incorporated into the films. We focused on the impact of growth conditions, such as reactor pressure, growth rate, and III/V ratio, on the surface morphology of these epitaxial films. The improvement of surface quality of III-V films on Si substrate associated with a reduction of dislocation density is important to achieve high-performance optoelectronics.

II. EXPERIMENT

The Si substrates used were 6 in. (001) with a 6° offcut toward the nearest {111} plane. Si0.50Ge0.50 buffers were commercially grown by ultrahigh vacuum chemical vapor deposition (the Lawrence Semiconductor Research Laboratory, Inc.) at a grading rate of ~10% Ge/μm and capped with 1 μm of Si0.50Ge0.50. Chemical mechanical polish was followed to remove ~500 nm of the Si0.50Ge0.50 capping layer to flatten the surface and to minimize surface roughness. Before loading the prefabricated Si0.50Ge0.50 wafers into an Aixtron Crius MOCVD reactor, they were cleaned in piranha solution (H2SO4:H2O2 = 3:1) for 10 min, followed by a 1 min hydrogen fluoride (HF) dip to remove any surface oxide. The SiGe wafers were placed in the reactor, and the subsequent temperature ramp-up procedure was done at 825 °C for 10 min to remove any moisture. For the SiGe growth, SiH4 and GeH4 were used as precursors and H2 was used as the carrier gas. The growth temperature was 750 °C, and the reactor pressure was 100 mbar. For the additional increase in the Ge content in the SiGe buffer layers, the same grading rate was used as for the prefabricated wafers. The grading was finished with a 500 nm Si0.29Ge0.71 capping layer, which was determined by symmetric (0 0 4) and asymmetric (2 2 4) reciprocal space maps (RSM). Then, the SiGe wafer was removed from the reactor and broken into 3 × 3 cm2 size pieces for the InGaP growth study.

Before loading the small pieces of SiGe into the reactor, they were dipped in HF for 1 min as the only cleaning step. The SiGe pieces were then baked in the reactor at 850 °C for 10 min under an arsine environment to create a double-atomic step surface which is critical for preventing the formation of antiphase boundaries (APB).7–10 Then, the temperature was ramped down to 650 °C to initiate InGaP growth. The Ga-rich InGaP samples with the layered structure shown in Fig. 1 were grown in a vertical chamber Aixtron Crius MOCVD (7 × 2 in. multiwafer reactor) with a close-coupled showerhead gas delivery system. Previous studies indicated that GaAs growth on Ge substrates is sensitive to the arsine partial pressure.11 Therefore, in order to grow APB-free III–V alloy on Ge, prior to the initiation of the InGaP growth a thin (about 10 nm) GaAs buffer layer was deposited using optimized growth conditions.11 Trimethyl gallium (TMGa) and trimethyl indium (TMIn) were used as the group III precursors, while arsine (AsH3) and phosphine (PH3) were used as the group V precursors. For the growth of Ga-rich InGaP, the reactor pressure was varied between 100 and 200 mbar, and the growth temperature was 650 °C, as measured by an in situ pyrometer. In an attempt to reduce hillock formation, the gas-phase V/III ratio was varied within the range of 44.3–402. Details of the growth conditions are shown in Table I.
The macroscopic composition, relaxation, and tilt behavior were determined by triple-axis high resolution x-ray diffraction (Bruker D8 Advance RSM) using the (004) and (-2-24) peaks. Steady-state photoluminescence (PL) measurements were performed at low temperature (10 K) using an Argon laser, a 1 m grating spectrometer, and a photomultiplier tube detector in the visible region. The sample temperature was controlled via a closed cycle helium cooled cryostat with a built-in resistive heating element. The PL spectra were achieved using spectrometer and silicon charge coupled device detector. An argon ion laser ($\lambda = 514$ nm) was used for excitation. The background spectrum was normalized using a piece of common silicon wafer. For comparison of the PL intensity, the optical setup was fixed, and the laser power was maintained to 5 mW (cw). Atomic force microscopy in tapping mode was used to measure the surface roughness with 5% errors in the height, density, and rms results. Nomarski microscopy was used to determine the hilllock density of the samples.

III. RESULTS AND DISCUSSION

The Si$_{x}$Ge$_{1-x}$ compositionally graded buffer on the Si substrate allowed an expansion of the lattice constant toward that of GaAs, which is lattice-matched to In$_{0.28-0.35}$Ga$_{0.65-0.72}$P. In our previous work, GaAsP films were prepared on SiGe virtual substrates to target emission in the green wavelength range. It was observed that the surface morphology of these materials was sensitive to the growth pressure and arsine preflow time.\textsuperscript{12} For closely lattice-matched InGaP films on Ge substrates, prior studies have found two different defects (i.e., arrowhead and asymmetric truncated pyramid hillocks) forming at the InGaP initiation layer due to imperfections in the surface step structure and carbon contamination on the surface.\textsuperscript{13} We previously observed that the surfaces of bulk GaAsP films grown directly on SiGe virtual substrates had pinholes.\textsuperscript{12} In this study, hillock formation was observed on the surface of bulk Ga-rich InGaP films on SiGe virtual substrates, as shown in Fig. 2, and this is similar to that observed for In$_{0.39-0.55}$Ga$_{0.45-0.61}$P on Ge or Si regions.

![SEM image of the surface of a bulk Ga-rich InGaP film on a SiGe virtual substrate (sample 305 as described in Fig. 7).](image)

![Symmetric (004) and asymmetric (-2-24) RSM images of a bulk Ga-rich InGaP film on a SiGe virtual substrate (sample 319).](image)

![Low temperature (10 K) photoluminescence spectra of InGaP films on a SiGe virtual substrate (samples 305, 313, 319, and 323).](image)

![Intensity and full width half-maximum of photoluminescence at low temperature (10 K) as function of hillock density for InGaP films on a SiGe virtual substrate.](image)
GaAs substrates. \(^{13,16,17}\) Hillocks with diameters in the range of 0.5–4 \(\mu\)m were observed for all Ga-rich InGaP films on SiGe virtual substrates.

The analysis of the RSM data was performed according to a procedure already outlined in the literature.\(^{14,15}\) Figs. 3(a) and 3(b) show the plotted RSM data for the Si\(_{x}\)Ge\(_{1-x}\) MBL in the region of the (004) and (-2–24) substrate peaks, with three distinct reciprocal lattice point maxima in accordance with the Si substrate, Si\(_{0.5}\)Ge\(_{0.5}\), Si\(_{0.29}\)Ge\(_{0.71}\), and the lattice-matched In\(_{0.34}\)Ga\(_{0.66}\)P. We observed that the In\(_{0.34}\)Ga\(_{0.66}\)P film and the top layer of the Si\(_{x}\)Ge\(_{1-x}\) MBL were almost fully relaxed \((\sim 93\%)\) and there was a large degree of tilt \((\sim 1.09\%)\) in the two orthogonal (110) directions. Low temperature PL (LT-PL) spectra of an In\(_{0.34}\)Ga\(_{0.66}\)P film (sample 305, 313, 319, and 323) was closely lattice matched to the Si\(_{0.29}\)Ge\(_{0.71}\) virtual substrate and showed a bandgap energy of 2.07–2.09 eV at 10 K, as shown in Fig. 4(a). For higher V/III ratios, the LT-PL peaks were slightly red shifted due to the composition and strain variation, or higher degree of CuPt\(_{12}\)-type ordering.\(^{18}\) For the lattice-matched In\(_{0.34}\)Ga\(_{0.66}\)P films on GaAs substrate, the high V/III ratio (i.e., group V-rich condition) facilitated the formation of \((2 \times 4)\) surface reconstruction, resulting in the CuPt\(_{12}\)-type ordering.\(^{17–19}\) The PL peak intensity (full width half maximum) of In\(_{0.34}\)Ga\(_{0.66}\)P film has been found to increase (decrease) with decreasing hillock density, due to dislocation associated with high hillock density levels [Fig. 4(b)]. The PL intensity is significantly reduced when the hillock density is higher than \(10^6\) cm\(^{-2}\).

The hillock densities of Ga-rich InGaP films grown using high V/III ratios (over 75.3) were about an order of magnitude higher than those of InGaP films grown using a low V/III ratio (under 75.3), as shown in Fig. 5 and Table I. The AFM data showed a clear minimum surface roughness for the InGaP film grown using a V/III ratio of 75.3. The higher V/III ratios resulted in higher hillock densities \((30.3\, to\, 30.1\, \times\, 10^4\, cm^{-2})\) and surface roughness \((4.67–9.03)\) values. Note that the samples grown with a high growth rate \((1.6\, \mu m/h)\) using a V/III ratio of 44.3 had about an order of magnitude higher hillock density than those produced with a low growth rate \((0.9\, \mu m/h)\), while the samples grown using a V/III ratio of 201 were not significantly influenced by the growth rate (Fig. 6). For Ga-rich InGaP grown using a V/III
Films on GaAs substrates. We observed a similar trend on SiGe virtual substrates with a bandgap energy of 2.07–2.09 eV at a low temperature were successfully grown using MOCVD. Further studies including Ga-rich InGaP films will be necessary to achieve the green range. We demonstrated that the growth conditions are the critical factor influencing the surface morphology of Ga-rich InGaP on SiGe virtual substrates. Decreasing the V/III gas phase ratio, growth pressure, and growth rate results in a reduction of the hillock density and size on the surface of the Ga-rich InGaP film. A higher growth pressure strongly increases the surface RMS roughness of these films. Ga-rich InGaP materials reported here exhibit hillock densities in the range of 30.3 × 10^4–30.7 × 10^5 cm^-2. In order to fulfill high-efficiency optoelectronics employing these materials, the hillock density of the films should be kept as low as possible. The bulk Ga-rich InGaP films on SiGe virtual substrates produced using optimized growth conditions are a potential material for improving the deposition of III–V epitaxial films on Si substrates for optoelectronic applications.

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IV. SUMMARY AND CONCLUSIONS

Bulk Ga-rich InGaP materials closely lattice matched to SiGe virtual substrates with a bandgap energy of 2.07–2.09 eV at a low temperature were successfully grown using MOCVD. Further studies including Ga-rich InGaP films will be necessary to achieve the green range. We demonstrated that the growth conditions are the critical factor influencing the surface morphology of Ga-rich InGaP on SiGe virtual substrates. Decreasing the V/III gas phase ratio, growth pressure, and growth rate results in a reduction of the hillock density and size on the surface of the Ga-rich InGaP film. A higher growth pressure strongly increases the surface RMS roughness of these films. Ga-rich InGaP materials reported here exhibit hillock densities in the range of 30.3 × 10^4–30.7 × 10^5 cm^-2. In order to fulfill high-efficiency optoelectronics employing these materials, the hillock density of the films should be kept as low as possible. The bulk Ga-rich InGaP films on SiGe virtual substrates produced using optimized growth conditions are a potential material for improving the deposition of III–V epitaxial films on Si substrates for optoelectronic applications.

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