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<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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Metalorganic chemical vapor deposition-regrown Ga-rich InGaP films on SiGe virtual substrates for Si-based III-V optoelectronic device applications

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Ga-rich InGaP materials are attractive applications for yellow-green spectral range optoelectronics such as light-emitting diodes and solar cells on silicon substrate. Bulk, Ga-rich InGaP films grown by metalorganic chemical vapor deposition on SiGe virtual substrates were investigated in the V/III compositional ratio range of 44.3–402 using chamber pressures from 100 to 200 mbar. These films were nominally lattice matched to the SiGe virtual substrate with a bandgap energy of 2.07–2.09 eV at low temperature (10 K). The authors show that the surface morphology of the Ga-rich InGaP films was dependent on the growth conditions, including the V/III gas phase ratio, pressure, and growth rate. By optimizing the growth conditions, the authors achieved improved surface morphologies of the Ga-rich InGaP films. The hillock density of the films produced using a V/III gas phase ratio of 44.3 and 75.4, a growth pressure of 100 mbar, and a growth rate of 0.9 \textmu m/h was about an order of magnitude lower (30.3–50 \times 10^4 cm^{-2}) than that observed using higher V/III gas phase ratios such as 201 and 402. An increase in luminescence efficiency of Ga-rich InGaP materials was observed when the hillock density is lower. The authors discuss the mechanisms of the hillock formation. © 2017 American Vacuum Society. [http://dx.doi.org/10.1116/1.4979272]

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_{1-x}Ge_{1-x}, GaAs_{1-y}P_{1,y}, or In_{1-z}Ga_{1-z}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_{0.5}Ga_{0.5}P (Refs. 1–3) and Al_{0.4}In_{0.6}P (Ref. 4) on GaP and GaAs substrates employing compositionally graded GaAs_{1-y}P_{1,y} and In_{1-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_{1-x}Ge_{1-x} compositionally graded buffer layers.
Although other research groups have demonstrated III-V solar cells on Si substrates employing compositionally graded Si$_{x}$Ge$_{1-x}$ MBL, it is challenging to produce high quality III-V alloys on a Si$_{x}$Ge$_{1-x}$ virtual substrate due to point defects, threading dislocations, and stacking faults. In this study, we report metalorganic chemical vapor deposition (MOCVD)-grown films of Ga-rich InGaP on Si substrates employing Si$_{x}$Ge$_{1-x}$ 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. Si$_{0.50}$Ge$_{0.50}$ 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 Si$_{0.50}$Ge$_{0.50}$. Chemical mechanical polish was followed to remove ~500 nm of the Si$_{0.50}$Ge$_{0.50}$ capping layer to flatten the surface and to minimize surface roughness. Before loading the prefabricated Si$_{0.50}$Ge$_{0.50}$ wafers into an Aixtron Crius MOCVD reactor, they were cleaned in piranha solution (H$_2$SO$_4$:H$_2$O$_2$ = 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, SiH$_4$ and GeH$_4$ were used as precursors and H$_2$ 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 Si$_{0.29}$Ge$_{0.71}$ 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 cm$^2$ 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). 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. 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. Trimethyl gallium (TMGa) and trimethyl indium (TMIn) were used as the group III precursors, while arsine (AsH$_3$) and phosphine (PH$_3$) 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.

### Table I. Growth conditions and resulting growth rate, hillock density, hillock height, and RMS roughness for bulk Ga-rich InGaP films on SiGe virtual substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V/III</th>
<th>Growth pressure (mbar)</th>
<th>Hillock density (cm$^{-2}$)</th>
<th>Hillock height (nm)</th>
<th>RMS roughness (nm)</th>
<th>Growth rate (μm/h)</th>
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<tr>
<td>299</td>
<td>201</td>
<td>100</td>
<td>$21.2 \times 10^4$</td>
<td>66</td>
<td>9.97</td>
<td>0.9</td>
</tr>
<tr>
<td>303</td>
<td>402</td>
<td>100</td>
<td>$30.1 \times 10^4$</td>
<td>60.4</td>
<td>9.03</td>
<td>0.9</td>
</tr>
<tr>
<td>305</td>
<td>402</td>
<td>200</td>
<td>$30.7 \times 10^4$</td>
<td>177</td>
<td>26</td>
<td>0.9</td>
</tr>
<tr>
<td>313</td>
<td>75.4</td>
<td>100</td>
<td>$48.5 \times 10^4$</td>
<td>34.9</td>
<td>4.65</td>
<td>0.9</td>
</tr>
<tr>
<td>318</td>
<td>44.3</td>
<td>100</td>
<td>$14.9 \times 10^4$</td>
<td>—</td>
<td>13.8</td>
<td>1.6</td>
</tr>
<tr>
<td>319</td>
<td>44.3</td>
<td>100</td>
<td>$30.3 \times 10^4$</td>
<td>54.9</td>
<td>7.61</td>
<td>0.9</td>
</tr>
<tr>
<td>323</td>
<td>201</td>
<td>100</td>
<td>$20.8 \times 10^5$</td>
<td>54.9</td>
<td>8.67</td>
<td>1.6</td>
</tr>
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Fig. 1. (Color online) Schematic showing the individual layers of the bulk Ga-rich InGaP film on a SiGe virtual substrate.
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. 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. We previously observed that the surfaces of bulk GaAsP films grown directly on SiGe virtual substrates had pinholes. 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 SiGe.
GaAs substrates. 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. 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 (~93%) and there was a large degree of tilt (~1.09\(^\circ\)) 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 CuPtB-type ordering. For the lattice-matched In\(_{0.5}\)Ga\(_{0.5}\)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 CuPtB-type ordering. 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 \(10^6 \text{ cm}^{-2}\).

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 (\(30.3 \times 10^4\) to \(30.1 \times 10^5 \text{ cm}^{-2}\)) 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...
ratio of 402, the hillock density was not dependent on the growth pressure, but the hillock size and root mean square (RMS) roughness showed a dramatic reduction with decreasing growth pressure, as shown in Fig. 7.

The origin of the hillock formation can be directly linked to the interface between the initiation GaAs layer and SiGe virtual substrate. We previously reported that the surface morphology of GaAs grown on Ge substrate revealed several pits due to step bunching occurring during the growth of the GaAs layer, which could also explain the hillock formation here. An alternative explanation is that the hillock formation arises from the tensile strain due to the lattice mismatch between the GaAs buffer layer and the InGaP films. There are many possible chemical interactions on the growth surface which can affect the hillock formation. The high V/III ratio inhibits surface diffusivity of group III ions, which may result in an increased hillock density on the Ga-rich InGaP surface when using high V/III ratios (i.e., higher than 200). Generally, high V/III ratios correlate with an improvement in the surface morphology of Ga-rich InGaP films on GaAs substrates. We observed a similar trend for Ga-rich InGaP using V/III ratios from 43 to 76. However, for V/III ratios over 201, the surface roughness was significantly increased owing to a reduction in the surface diffusivity. A microstructural investigation, using transmission electron microscopy, for example, will be required to elucidate this point.

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-richer 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 $30.3 \times 10^4$–$30.7 \times 10^5$ cm$^{-2}$. In order to fulfill high efficiencies 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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