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Nucleation-related defect-free GaP/Si(100) heteroepitaxy via metal-organic chemical vapor deposition

T. J. Grassman,1,2 J. A. Carlin,3 B. Galiana,3 L.-M. Yang,2 F. Yang,2 M. J. Mills,2 and S. A. Ringel1,3

1Department of Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio 43210, USA
2Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio 43210, USA
3Institute for Materials Research, The Ohio State University, Columbus, Ohio 43210, USA

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GaP/Si heterostructures were grown by metal-organic chemical vapor deposition in which the formation of all heterovalent nucleation-related defects (antiphase domains, stacking faults, and microtwins) were fully and simultaneously suppressed, as observed via transmission electron microscopy (TEM). This was achieved through a combination of intentional Si(100) substrate misorientation, Si homoepitaxy prior to GaP growth, and GaP nucleation by Ga-initiated atomic layer epitaxy. Unintentional (311) Si surface faceting due to biatomic step-bunching during Si homoepitaxy was observed by atomic force microscopy and TEM and was found to also yield defect-free GaP/Si interfaces. © 2013 AIP Publishing LLC.

The ability to grow high quality epitaxial GaP layers on Si has been of interest for decades, largely due to the desire to use a GaP/Si heterostructure, with its small but non-negligible lattice constant mismatch (0.37% at 300 K), as a method to achieve III-V/Si integration. Integration is of interest as an enabling pathway for the production of high-efficiency, monolithically integrated III-V/Si photovoltaics, as well as Si-based photonic, optoelectronics, and high-speed microelectronics, since a virtual GaP (on Si) substrate would support subsequent metamorphic epitaxy based on GaAsP and GaInP alloys. However, the integration of GaP with Si is not trivial, and incompatibilities of intrinsic materials properties, such as lattice mismatch, interfacial heterovalency (polar/non-polar), thermal expansion mismatch, and surface/interface chemistry, have provided substantial barriers to success and a general inability to sufficiently suppress the resulting electrically active crystalline defects, including anti-phase domains (APDs), stacking faults (SFs) and microtwins (MTs), and dislocations.

However, recent molecular beam epitaxy (MBE) based work focusing on the application of surface and interface chemistry knowledge to the careful control and design of the Si substrate preparation and GaP nucleation has demonstrated that these heterovalent nucleation related defects (APDs, SFs, MTs) can indeed be simultaneously and entirely suppressed, and nucleation-defect free GaP/Si has indeed been achieved.

For this, a combination of Si(100) substrate vicinality and preparation to yield a pristine, biatomic step reconstructed surface, well-controlled GaP nucleation via migration enhanced epitaxy, and an overall consideration of epitaxial film mechanics and heterovalent interface properties in epitaxial structure design was used to produce high-quality heteroepitaxial GaP/Si layers capable of supporting further III-V epitaxy for device applications, particularly photovoltaics.

Similarly, much recent progress has also been made via metal-organic chemical vapor deposition (MOCVD) growth methods for such GaP/Si heteroepitaxy, wherein an insightful surface preparation procedure on nominally exact-oriented Si(100) substrates, along with an atomic layer epitaxy (ALE) nucleation approach, has been shown to yield GaP (and subsequent high-quality Si-matched BGaP and GaNP) films free of SF and MT defects, although with a relatively sparse population of internally self-annihilating APD defects still present.

Nonetheless, III-V alloys that are lattice-matched to Si are inadequate for use in most technological applications where an integrated III-V/Si materials system would be desirable. In many cases, such as where metamorphic (lattice-mismatched) III-V epitaxy is needed to provide access to target materials, the integrated GaP/Si system is expected to serve as a growth template or virtual substrate. However, the existence of interfacial APD disorder is likely to inhibit dislocation glide, preventing the efficient relaxation of the misfit strain between the GaP and Si, any such interference with interfacial dislocation glide will likely result in the generation of excess dislocation density, which can be detrimental to ensuing integrated devices.

Here, GaP/Si(100) heterostructures grown by MOCVD that are simultaneously devoid of SFs, MTs, and APDs are reported. The approach is generally modeled after the authors’ previously developed MBE-based methodology. A similar combination of intentional Si(100) substrate misorientation to yield a biatomic surface step reconstruction, Si epitaxy prior to GaP nucleation to provide a pristine growth surface, and the use of a Ga-initiated ALE nucleation process was found to produce GaP films free of all nucleation-related defects (APDs, SFs, MTs). Additionally, the Si epitaxy conditions used in this work yielded unintentional step-bunching, leading to the formation of (311) surface facets, which are also found to be benign with respect to GaP nucleation.

All GaP and Si growth reported herein was performed in a 3×2 in. Aixtron MOCVD system with a close-coupled showerhead (130 mm inject area diameter). Precursors used for the associated growths were silane (SiH4), triethylgallium (C3H7Ga, “TEGa”), and tert-butylphosphine (C8H17P, “TBP”). The typical working pressure for all growth modes reported here was 150 millibars. In-situ monitoring of the
growths was performed via reflectance/photometry, while post-growth analysis included atomic force microscopy (AFM), high-resolution triple-axis X-ray diffractometry (XRD), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM).

A variety of (100)-oriented Si substrates were used for the growths described herein, including wafers with 50.8 mm and 76.2 mm diameters and intentional offcuts of 4° and 6° in the [011] direction, all with equivalent results. Prior to loading into the reactor, the substrates were etched in a 1:100 HF:DI H2O solution to remove the native oxide and provide a H-passivated surface. As in the authors’ previous MBE-based GaP/Si work, a thin (~90 nm here) Si homoepitaxial cap layer was grown in-situ on the Si substrates at ≥760 °C, immediately prior to any III-V nucleation, as a means to bury any persistent and likely problematic, surface contaminants (particularly carbon); this temperature is also sufficient to yield the biatomic step surface reconstruction.

Also following the previous MBE-based work, GaP nucleation on the pristine Si surface was achieved via low-temperature (450 °C) ALE. Low-temperature reactive TEGa and TBP precursors were used for the ALE nucleation, with the TEGa pulses carefully calibrated (via AFM) to give exactly full monolayer coverage. To prevent adverse Si-P reactions, the ALE GaP nucleation was Ga-initiated. Following each TEGa dose and purge, the surface was exposed to a flow of TBP, followed by a purge and short pause to allow for reaction equilibration. A total of 25 GaP ALE cycles was used for the growths reported here. After ALE-GaP nucleation, the substrate temperature was increased under TBP flow to ~580 °C, where a 250 nm thick, but otherwise unoptimized, homoepitaxial GaP cap layer was grown via standard MOCVD process to provide a film with sufficient bulk cohesion to survive subsequent high-temperature exposure, thereby producing a true GaP/Si virtual substrate.

Figure 1(a) presents AFM scans of a homoepitaxial (~90 nm) Si surface on a 6° offcut Si(100) substrate (with no GaP growth). Evident on the Si surface is a quasi-periodic “ripple” structure, with vertical and lateral length scales larger than expected for biatomic stepping on a vicinal substrate, suggesting some sort of step bunching; the surface appears, otherwise, to be atomically smooth, with a maximum calculated root-mean-square (RMS) roughness (from a 500 × 500 nm² image) of 0.39 nm, equal to that of the pre-epitaxy Si surface. Indeed, cross-sectional TEM/STEM (X-TEM/STEM) analysis of such structures capped with subsequent GaP growth (shown in Figure 2 for a similar 6° offcut substrate) reveal the existence of tall (~4 nm), step-like structures with wide (~50 nm), flat terraces. The smooth step sidewall faces are found to lie at an angle of about 25° from the (100) surface, consistent with the formation of (311) facets via biatomic step bunching, as reported elsewhere. These (311) facets are the result of anisotropies in the Si adatom surface and step edge diffusion kinetics and are found to manifest under certain combinations of growth and/or annealing conditions (temperature, growth rate, substrate misorientation). For the sake of simplicity, and because results obtained from 4° offcut substrates were effectively identical to those from 6° offcut, with only slight differences in step periodicity and height, only 6° offcut results are presented.

Fig. 1(b) presents an AFM scan of a GaP nucleation layer grown by ALE on a 6° offcut Si(100) substrate identical to that shown in Fig. 1(a). The image indicates a smooth (0.60 nm RMS surface roughness), continuous film with no Volmer-Weber type island formation and which maintains much of the underlying Si ripple structure. Fig. 1(c) presents AFM data from a 250 nm thick GaP layer grown via low-temperature (580 °C) MOCVD on the ALE-grown GaP/Si nucleation layer. These as-grown films present flat and
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samples were imaged via both TEM and STEM in zone-axis and two-beam $g(200)$ and $g(220)$ [not shown] conditions to provide a thorough analysis of the heterovalent interface. As displayed in Fig. 2(a), and effectively identical to the results obtained previously via MBE, the only defects evident in any such sample were the expected misfit/threading dislocations due to growing beyond the critical thickness (approximately 40–90 nm at growth temp), indicating that the heteroepitaxial nucleation and growth process used was indeed successful at fully preventing the formation of all nucleation related defects, including SFs, MTs, and even small-scale APDs. However, not observed in the MBE work are the periodic, large-scale step features that can clearly be seen via zone-axis STEM imaging, such as in Fig. 2(b); high-resolution STEM imaging of these steps, provided in Fig. 2(c), shows the $25^\circ$ inclined (311) step-edge faceting.

While the (311) faceted step-bunching was an unintended result of the epitaxial Si growth conditions used for this work, its presence, and any potential impact (or lack thereof) on the GaP/Si heterovalent interface, is nonetheless interesting and worth consideration. Because the (311) faceting is formed via the bunching of biatomic steps, the resulting large-scale steps would be expected to possess an even number of atomic layers (i.e., $h_{\text{rep}} = 2n \times d_{\text{Si}}/4$), a necessity for the preclusion of APD nucleation due to shifted III-V lattice registry. As such, STEM image based measurements reveal even-numbered step heights on all such faceted steps measured, with a median value of $8d_{\text{Si}}$ on the 6° samples. However, slope (i.e., height/width) analysis of the faceted steps indicates that, in the case of the 6° offcut samples, only $\sim 3.8^\circ$ worth of misorientation is actually accounted for by the large-scale steps, suggesting that the wide terraces themselves still possess $\sim 2.2^\circ$ worth of misorientation, which is still sufficient to ensure full biatomic stepping to prevent APD nucleation.

Of particular interest is the GaP/Si interface at the (311) facets. Since there are no observable nucleation-related defects (APDs, SFs, MTs) at these facets, they must be considered benign with respect to the heterovalent nucleation. Indeed, the atomic configuration of the Si(311) surface, with alternating rows of 2- and 3-fold coordinated Si surface atoms (i.e., with two and one dangling bonds, respectively, as depicted in Figure 3), should yield a site-selective chemistry conducive to APD-free heterovalent epitaxy at these facets, consistent with growth on Si(211) and Si(311) surfaces as previously reported. Therefore, the serendipitous combination of both biatomic stepping and (311) faceting on the vicinal Si(100) surface, which on their own should be sufficient for the prevention of APDs, appears to work in a complementary (or at least non-conflicting) manner, enabling the growth of GaP on Si(100) free of all nucleation-related defects.

The results presented herein demonstrate the growth, by MOCVD, of GaP on Si(100), free of all heterovalent nucleation-related defects, including APDs, SFs, and MTs. The same surface science guided approach previously demonstrated via MBE for the suppression of nucleation-related defects—the combination of substrate vicinality, pristine surface preparation by homoepitaxial Si epitaxy, and Ga-initiated ALE nucleation—was shown to be equally
effective for MOCVD-based growth. A particularly interesting aspect of the MOCVD-based growths not seen in the MBE-based work was the formation of (311) faceted step-bunches which were found to yield defect-free GaP/Si interfaces, providing an unanticipated simultaneous demonstration of an alternative heterovalent integration mechanism. This work represents a critical validation of methodology transition between the MBE and MOCVD growth techniques, providing a pathway for the production of heteroepitaxially integrated III-V/Si structures, with applicability toward a range of important device technologies, via standard commercial fabrication approaches.

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