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Epitaxial growth of three dimensionally structured III-V photonic crystal via hydride vapor phase epitaxy

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Three-dimensional (3D) photonic crystals are one class of materials where epitaxy, and the resultant attractive electronic properties, would enable new functionalities for optoelectronic devices. Here we utilize self-assembled colloidal templates to fabricate epitaxially grown single-crystal 3D mesostructured GaIn1−xP (GaInP) semiconductor photonic crystals using hydride vapor phase epitaxy (HVPE). The epitaxial relationship between the 3D GaInP and the substrate is preserved during the growth through the complex geometry of the template as confirmed by X-ray diffraction (XRD) and high resolution transmission electron microscopy. XRD reciprocal space mapping of the 3D epitaxial layer further demonstrates the film to be nearly fully relaxed with a negligible strain gradient. Fourier transform infrared spectroscopy reflection measurement indicates the optical properties of the photonic crystal which agree with finite difference time domain simulations. This work extends the scope of the very few known methods for the fabrication of epitaxial III-V 3D mesostructured materials to the well-developed HVPE technique.

I. INTRODUCTION

Optoelectronic devices including zero-threshold lasers,1 low-loss waveguides,2,3 light-emitting diodes (LED),4 and photovoltaic (PV) cells5 have long benefited from structuring in multiple dimensions on microscopic length scales to enhance or provide new properties. However, preserving crystal epitaxy, a general necessity for good optoelectronic properties to minimize undesired recombination and other losses, while imparting a complex three-dimensional structure, remains a significant challenge in the development of functional 3D photonic crystal devices. There are many pathways to build a complex 3D structures from amorphous or polycrystalline materials including electrochemical deposition, anisotropic dry etching, wafer bonding, and layer-by-layer micromanipulation techniques.6–10 But as far as we are aware, other than our recently reported 3D Cu2O inverse opal grown by electrodeposition,11 only two semiconductors, GaAs and GaN, have been fabricated as 3D structured single-crystal, in both cases by means of a selective area epitaxy chemical vapor deposition (CVD) process.12,13 Expansion of the materials list to include other potentially functional epitaxial materials that can be grown in a 3D mesostructured form, with the possibility of further reduction in defect density would be desirable.

III-V semiconductors such as GaAs, GaInP, and InP are considered attractive candidates for optoelectronic devices due to their optimal band gaps and high absorption coefficients. In addition to photovoltaic application,14 they have been widely utilized in solid state lasers, LEDs, and optical waveguides.15–18 We are particularly interested in hydride vapor phase epitaxy (HVPE) for III-V semiconductor growth. It uses group-III chlorides and group-V hydrides as precursors,19 and operates at near-equilibrium conditions and hence high surface selectivity of III-V semiconductor growth can be achieved even in the case of nanosized openings,20 which is critical when our 3D mask is present. An indication that growth through a 3D mask might be successful was provided by prior work on reducing threading dislocations (which are responsible for property deterioration)21 during heteroepitaxial growth of III-V semiconductors on substrates with some degree of lattice mismatch. HVPE selective growth of III-V compounds through a nanostructured mask was used to reduce the threading dislocation density in heteroepitaxy, and no growth on the mask was observed.22 Here, we demonstrate the successful heteroepitaxial growth of a 3D GaInP photonic crystal on a InP(001) substrate coated with a self-assembled silica colloidal crystal template by HVPE. The epitaxy is preserved during the growth through the complex internal pore geometry of the template as confirmed by X-ray diffraction and high resolution transmission electron microscopy.

II. EXPERIMENT

600 nm diameter silica colloidal spheres were fabricated using the methods described by Stöber et al.23

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followed by several regrowth cycles. Prior to colloidal crystal assembly, we heat-treat the spheres for 6 h at 600 °C to avoid sphere densification that may lead to cracking of the opal structure during the HPVE.24 We then cut and dip one side polished InP(001) single crystal substrate in 98% H2SO4 for 60 s before colloidal crystal growth to create a metal and native oxide free epi-ready surface. A modified vertical deposition25 method that employs a temperature gradient26 was utilized to deposit colloidal crystal films on the InP substrate. In brief, InP substrates were placed at a 20° angle in a 20 ml scintillation vial containing 4–5 g of ethanolic colloidal dispersion (4–5 wt. %) of the 600 nm silica microsphere. After leaving the vials in an incubator (Fisher, Isotemp 125D) at ~45°C overnight, the silica spheres self-assembled into 5–8 layers of face centered cubic structure on InP substrates (Fig. 1(a)). GaInP selective growth was performed in a commercial low-pressure hydride vapor phase epitaxy reactor (LP-HVPE) at 20 mbar and 590 °C. GaCl and InCl were used as group III precursors, which were formed by flowing HCl gas over molten Ga or In metal in quartz boat heated at 740 °C. PH3 flow of 120 sccm, InCl flow of 20 sccm, GaCl flow of 2 sccm, and the total flow of 900 sccm in the reactor including the nitrogen carrier gas were used in this work. This set of growth parameters gives the solid composition of Ga0.45In0.55P on a planar GaAs substrate as confirmed by a separate run. We noticed that the appropriate temperature window used to grow high quality inverse opals was small and occasionally needed to be experimentally adjusted. We only selected region with high-quality (closely packed) templates with 5–6 opal layers for characterization of reflection spectroscopy along with scanning electron microscopy (SEM). The silica template is etched away by a 3 min dip in 25% hydrofluoric acid before optical characterization after the removal of the GaInP overlayer (see below) by inductively coupled plasma reactive ion etching (ICP-RIE) using a mixture of Cl2/Ar at 60 °C for 10 min.

SEM is utilized to characterize the morphology of the silica colloidal crystal template and 3D GaInP infilling after HVPE growth. X-ray diffraction is employed to study the crystallinity and composition of the resulting 3D mesostructured GaInP using a Philips X’pert MRD system. Structural defect and epitaxy relationship between film and substrate are further revealed by high resolution transmission electron microscopy (HRTEM) and scanning TEM (STEM) with a JEOL 2010F facility 2100 TEM equipped with a LaB6 gun and operated at 200 kV. Z-contrast imaging in a STEM was also performed to determine the nature of defects. STEM images were obtained with a JEOL 2200FS equipped with a CEOS probe corrector and operated at 200 kV. Reflectance spectra of the GaInP photonic crystal were studied using a Vertex 70 Fourier transform infrared spectroscopy coupled with a Bruker Hyperion microscope and compared with finite difference time domain (FDTD) method simulation result calculated using the free MIT Electromagnetic Equation Propagation software.27,28

III. RESULTS AND DISCUSSION

The SEM cross-section image in Fig. 1(a) shows a representative silica colloidal crystal assembled on an InP substrate. 5 layers of close packed opal structure were obtained using the procedure described above. Fig. 1(b) shows a 3D GaInP layer epoxially grown on the InP(001) substrate through and above a silica colloidal template. It can be seen that the grown GaInP material conforms to the complex geometry of the template and continues growing, forming a thick overlayer on the top. Except for some small regions (see Fig. S1),29 most of the template is covered with...
overgrown GaInP propagated from the bottom. The small uncovered region is believed to be caused by either point defects of the template structure which could change the local reaction rate during the HVPE around it or nucleation occurs on the thick template surface as discussed below. The cross section and plain view of the mesostructured GaInP after the removal of the overlayer and the silica template are shown in Figs. 1(c) and 1(d). The GaInP inverse opal structure obtained closely matches the pore structure of the initial opal due to the selectively of the HF etching process; however, the top surface is relatively rough due to the ICP-RIE used to remove the GaInP overlayer.

Traditional 2D selective epitaxial growth relies on the preference for growth on the semiconductor substrate rather than the mask material.\textsuperscript{30,31} When applied to planar device fabrication, if a small amount of nucleation occurs on the mask surface the nuclei are typically removed when the mask is etched. However, if nucleation occurs on the surface of our 3D masks a polycrystalline film of 3D structure will result, as the nuclei penetrate downward into the template\textsuperscript{12} resulting in incorporation of polycrystalline material into the 3D structure. Since diffusion of the precursors through the 3D template is reduced in comparison with the bulk gas phase, an increased partial pressure of the source materials over the 3D mask as the number of layer increases may affect the nucleation behavior.\textsuperscript{12} This is consistent with our observation that the surface nuclei tend to form at edge region of the silica template where the layer is thicker than center. In experiment, we chose to use 5–6 layer of opal template in the HPVE growth since thicker samples with more than 10 layers usually are covered by polycrystalline surface nuclei.\textsuperscript{32}

To characterize the crystallite structure and confirm the epitaxy of the 3D mesostructured GaInP, we first performed a XRD 2\theta/\theta scan. Fig. 2(a) shows a 2\theta/\theta scan result from 10\degree to 90\degree of the GaInP layer on InP (001) wafer with diffraction peaks labeled according to standard JCPD reference data (file No. 04-002-1198 for Ga0.5In0.5P and No. 04-004-8072 for InP, respectively). Besides the InP substrate peaks, only two distinct peaks at around 31.3\degree and 65.2\degree corresponding to (002) and (004) crystal plane of Ga0.5In0.5P are detected, indicating the formation of a highly textured 3D GaInP deposit with its [001] orientation aligned with the substrate [001] direction. The two observed GaInP diffraction peaks are broadened with FWHM of around 0.40\degree and 0.90\degree, respectively, based on the detailed XRD scan close to each of them (see Fig. 2(b) for the magnified GaInP (002) peak). The rocking curve of the GaInP (002) peak as shown in Fig. 2(c) has a FWHM of 1.47\degree but does not show noticeable double-peak shape through curve fitting. GaInP peaks in both the scans are wider than those of the GaInP thin film grown by molecular beam epitaxy (MBE) on GaAs or InP but comparable with those of the film grown by liquid phase epitaxy, which also is an equilibrium process, indicating a relative close resemblance to the quality of the materials fabricated by the latter method.\textsuperscript{33–35} Besides the instrumental factors, the Bragg peak width of the epitaxial thin film depends on material properties including: the finite size of the scattering crystal, strain gradients,\textsuperscript{36} chemical composition distributions, and crystal defects such as dislocations.\textsuperscript{37} Peak broadenings reported for epitaxially grown GaInP on (001) GaAs by both liquid phase epitaxy and metalorganic vapor phase epitaxy (MOVPE) have been primarily attributed to the composition separations (inhomogeneity) in the grown film induced by lattice stress due to the combination of lattice mismatch during growth and the differences of the thermal expansion coefficient during cooling.\textsuperscript{34,38,39} Considering the similarity of the growth process of our method and MOVPE, composition separation could be a reason for the observed peak broadening, but this hypothesis does not rule out the possible contributions of strain gradients and structural imperfections.

In order to gain further insight into the composition distribution and strain relaxation condition in the 3D GaInP layer, XRD reciprocal space mapping (RSM) measurements were performed. Figs. 2(d) and 2(e) show the logarithmic scale diffraction intensity maps in the vicinity of the InP (004) (symmetric scan) and (115) (asymmetric scan) reflection peaks in a plane spanned by [110] and [001] directions of the substrate. Symmetric (004) RSM (Fig. 2(d)) shows the presence of a GaInP film peak indexed as (004) above that of the InP (004). A Gaussian fit of the GaInP diffraction peak in the direction perpendicular and parallel to [001] vector reveals an out-of-plane lattice constant \(c\approx0.57056\) nm which gives a perpendicular lattice mismatch of −2.67\% as compared with the substrate in the same direction (0.58688 nm), and a negligible crystallographic tilt of −0.0029\degree. Asymmetric (115) RSM studies near the (115) diffraction condition of the substrate (Fig. 2(e)) show the presence of a relaxed film peak indexed to be the (115) diffraction condition that enables calculation of the in-plane lattice constant \(a\approx0.57242\) nm which has lattice mismatch of −2.18\% and a mosaic spread of 1.27\degree. We also performed RSMs in the vicinity of InP (002) and (224) (not shown here) where lattice constants of \(c\approx0.57120\) nm and \(a\approx0.57407\) nm were obtained. From the above RSMs, the average lattice constants are \(c\approx0.57088\) nm and \(a\approx0.57324\) nm. If we assume the lattice structure is only affected by the chemical composition, the in-plane and out-of-plane lattice parameters of \(c\) and \(a\) depend on the mole fraction \(x\) in Ga\(_x\)In\(_{1-x}\)P as given by Vegard’s law:\textsuperscript{40}

\[
c(x) = x_{\text{GaP}} + (1 - x)_{\text{InP}}, \tag{1}
\]

\[
a(x) = x_{\text{GaP}} + (1 - x)_{\text{InP}}. \tag{2}
\]

Using the GaP and InP lattice constants \(a_{\text{GaP}} = 0.54505\) nm and \(a_{\text{InP}} = 0.58688\) nm, together with the averaged value of measured \(a(x)\) and \(c(x)\) given above, we could calculate the approximate Ga\(_x\)In\(_{1-x}\)P mole fraction \(x\approx0.38\) (from the lattice parameter \(c\)) or \(x\approx0.32\) (from the lattice parameter \(a\)). If we consider the misfit strains in the epilayer assuming a tetragonal distortion in a biaxially strained crystal (see discussion below), the average mole fraction \(x\) could be calculated as:\textsuperscript{41}

\[
x = \frac{ac(1 + \nu) - ac_{\text{GaP}} - ac_{\text{InP}}}{ac_{\text{InP}} - ac_{\text{GaP}} + \frac{ac_{\text{GaP}} - ac_{\text{InP}}}{c} - \frac{ac_{\text{InP}} - c_{\text{GaP}}}{c}}, \tag{3}
\]
where \( \nu \) is the Poisson’s Ratio of InP. Taking \( \nu = 0.36 \), then this formula gives \( x = 0.36 \) which lies between the two values calculated from the Vegard’s rule. The deviation between the solid composition obtained here and the nominal mole fraction of \( x = 0.45 \) might be caused by various facet planes formed during SAG of GaInP in 3D template. The In-rich composition could be due to the different incorporation efficiencies of Ga and In in different crystalline planes during GaInP selective growth. Such GaInP composition shift toward In-rich caused by selective growth has been observed in growth on GaAs substrate.32

We also observed broadening of the reciprocal lattice point (RLP) compared to the sharp substrate peaks. Typically, for epitaxial semiconductor alloy films, the elongation of a RLP perpendicular to the diffraction vector is a measure of the mosaicity caused by structural imperfections in the crystal such as misfit dislocations and stacking faults, while the elongation of RLP parallel to the diffraction vector is related to the variation in lattice constant.43 Although both the strain and composition gradients can cause the variation of the lattice parameter, the two factors lead to the RLP elongation in different directions in the asymmetric RSM.44,45 To better investigate the strain situation in the 3D GaInP layer, we drew a vertical line crossing the substrate RLP center and an inclined line which connects the origin of reciprocal space with the (115) substrate RLP corresponding to the fully strained and fully relaxed states of the epilayer, respectively.

In both of RSMs (Figs. 2(d) and 2(e)) of our sample, the

FIG. 2. (a) XRD overview 2θ/ω scan of the 3D GaInP grown on InP(001) single crystal wafer and (b) fine 2θ/ω scan around InP (002). (c) Rocking curve with 2θ fixed at of GaInP (002). (d) Reciprocal space mapping at the vicinity of the InP (004) peak and (e) (115) peak with fully strained (black dashed dotted), fully relaxed (black dashed), and relaxation (red dashed) lines. XRD pole figures obtained at the orientation of GaInP (022) (f) and (113) (g).
GaInP RLPs are more broadened in the direction perpendicular to the diffraction vector than that in the direction parallel to it with their peaks FWHM ratios along the two directions to be around 1.64 and 1.43 in the (004) and (115) RSMs, respectively. This suggests that the structural defects (stacking faults and dislocations) are more favorable than the composition variation in the accommodation of lattice mismatch in the epitaxial growth along the [001] direction. The (115) RSM (Fig. 2(e)) demonstrates a quasieLLiptical iso-intensity contours of GaInP RLP with its main axes parallel and perpendicular to an [115] direction in the map implying the absence of both large-scale strain gradients and statistically randomly distributed elastic strains within the epilayer. To further rule out the effect of the strain gradients, a relaxation line with its angle between the Qz axis, \( \alpha(x) \), calculated from expression below is drawn in Fig. 2(c) (Ref. 45)

\[
\alpha(x) = \tan^{-1}\left( \frac{\tan(\phi)}{D(x)} \frac{4(l^2 + h^2)}{1\sqrt{4/3(h^2 + h + l)^2}} \right),
\]

where \( \phi \) is the angle between the surface normal and the (hkl) plane given by the expression

\[
\tan(\phi) = \frac{c}{a} \sqrt{\frac{4(h^2 + h + l)^2}{3l^2}}
\]

and \( D(x) \) is the anisotropy factor determined by

\[
D(x) = -\frac{\varepsilon_{zz}(x)}{\varepsilon_{xx}(x)}.
\]

Here, \( \varepsilon_{ii} \) are the strain components defined as \( \varepsilon_{zz} = (c - c_0(x))/c_0(x) \) and \( \varepsilon_{xx} = (a - a_0(x))/a_0(x) \), where \( c_0 \) and \( a_0 \) are the fully relaxed lattice parameters given by Vegard’s law. It can be seen that the GaInP (115) RLP is slightly shifted from the fully relaxed line with the calculated \( \alpha \approx 41.2^\circ \) which indicates a very weak elongation along the relaxation line compared with the elongation perpendicular to the [115] direction; this suggests a negligible strain gradient and a nearly full relaxation of the epilayer within the 3D mesostructured template.

Texture of the epitaxial layer was also studied by the pole figure (Figs. 2(f) and 2(g)) measured at the Bragg angle of \( GaxIn1_{-x}P \) (022) and (113) reflection with XRD detector placed at \( 2\theta = 44.70^\circ \) and 52.96\(^\circ\), respectively. Sharp diffraction spots located at an inclination angle of \( \psi = 45.0^\circ \) with a fourfold symmetry pattern in Fig. 2(f) correspond to {022} lattice planes of GaInP, and fourfold symmetric sharp spots at 25.2\(^\circ\) in Fig. 2(g) correspond to {113} planes. The fact that there are four accurately uniformly spaced peaks in the two pole figures reveal the fourfold symmetry of the film, confirming a good in-plane alignment between the GaInP film and the InP substrate. The {002} pole figure also shows several additional peaks at \( \phi = 19.2^\circ \) that are suspected to be from the {822} family of planes resulting from {022} twinning about [111]. In fact, for zincblende crystals, the [111] planes has the largest inter-planar spacing and the lowest Peierls stress which facilitate the formation of twinning\(^{46}\) that occurs frequently in the III–V nanostructures, such as nanowires\(^{47,48}\) and 3D GaAs grown through colloidal template.\(^{12}\)

The most important feature of the 3D selective area epitaxy process is that growth begins at the substrate and extends upwards while preserving epitaxy, enabling formation of chemically and electrically complex heterostructures. We performed cross-sectional transmission electron microscopy in addition to x-ray diffraction to further characterize the GaInP epilayer and any structural defects in the material. The TEM sample was prepared by mechanical polishing with diamond lapping films, which was then followed by ion milling using 3.0 and 2.0 kV Ar ions at a glancing angle of \( \pm 7^\circ \). The TEM sample was cooled to liquid nitrogen temperature to minimize ion beam induced damages. Figs. 3(a) and 3(b) display cross-sectional TEM images near the interface between the epitaxial 3D GaInP and the InP substrate. The congruence of the lattice fringe and the aligned selective area electron diffraction (SAED) patterns of 3D GaInP film and the InP substrate in the HRTEM and STEM images (see Fig. 3(b), Figs. S2 and S3)\(^{29}\) together with the previously shown RSMs (Fig. 2) confirm the epitaxial growth relation within a cube-on-cube fashion (001)GaInP\([100]\)InP, and [100]GaInP\([100]\)InP. The DF-TEM recorded using the (002) reflection reveals extensive crystal defects. The planar defects originating from the interface are readily identified as [111] type stacking faults, which typically form the so-called Lomer–Cottrell lock. The atomic resolution STEM of Fig. 3(d) shows a stacking fault with a missing lattice plane in the 3D GaInP resulting from the high mismatch stress at the interface during HVPE growth and the thermal stress. Besides the stacking faults, the strain in the lattice-mismatched III-V semiconductor epitaxial growth is accommodated by creating 60° type misfit dislocations once a certain critical thickness (typically few tens of nm for GaInP) has been exceeded. Due to the presence of local strain field associated with the compositional modulation occurred in the GaInP epilayers and the fact that the 60° dislocations are at nearly edge-on position, the dislocations are not so readily recognized in the DF-TEM. But they can be revealed by STEM as depicted in Figs. S2 and S3.\(^{29}\) We noticed that there is no preferred orientation among [110] or [110] misfit dislocation lines which implies no asymmetry in the resolved shear stress on different [111] glide planes. Lomer dislocations, as have been found in the MBE grown lattice-matched \( GaxIn1_{-x}P/GaAs \) heterostructure,\(^{49}\) have also been observed in our 3D GaInP as shown in Fig. S3.\(^{29}\) In epitaxial layers of ternary III-V compounds such as \( Ga_{x}In_{1-x}As \) and \( Ga_{x}In_{1-x}P \) with zinc blende crystal structure certain growth conditions may lead to an ordered structure (such as the CuPt ordering), where the Ga and In atoms are distributed on the group-III lattice (111) plane periodically.\(^{50,51}\) The ordered lattice produces extra diffraction reflections due to the added element of periodicity that changes the structure factor of the crystal that could be detected by TEM.\(^{52,53}\) In our [110] zone axis SAED patterns (Fig. 3(b), insets) from a cross sectional sample of GaInP area, however, there are no additional spots that would correspond to an ordered superstructure which indicates an absence of atomic ordering. The lack of such ordering may
be correlated to the composition change of the GaInP approaching InP near the interface which also implies that the strain relaxation mechanisms of the lattice mismatched epitaxy do not necessarily depend on ordering.\textsuperscript{54}

The optical properties of the 3D mesostructured GaInP photonic crystal were studied by reflectance spectra measurements using a Fourier transform infrared spectrometer with a $10 \times$ objective lens (N.A. = 0.25) which detects an area of $\sim 250 \mu m$ diameter on the sample. The GaInP photonic crystal was represented by the appropriate dielectric constant data in the FDTD simulation.\textsuperscript{55} Fig. 4 shows typical normal incidence reflectance spectra and FDTD reflectance simulations of the GaInP photonic crystal after the removal of the silica microsphere template depicted in the SEM images of Figs. 1(c) and 1(d). The measured peak at around $1.55 \mu m$ is not present in the reflectance collected from a flat GaInP film (Figs. 4(a), inset), and matches well with FDTD simulations where we modeled 3D GaInP as inverse face-centered cubic lattice of close-packed 600 nm voids. This result serves as an evidence of complete material conversion of the silica opal into GaInP inverse opal without large amount of unfilled voids which is in agreement with what is observed in SEM. The measured reflectance peak intensity is lower than the calculated result, which is to be expected considering the existence of defects in the opal template, and surface roughness due to the ICP-RIE. We notice that the choice of the silica microsphere size is arbitrary in our experiment and a wide range of template feature size should be possible for the 3D GaInP photonic crystal fabrication.

**IV. CONCLUSION**

In summary, we have developed a new colloidal template directed approach to fabricate epitaxial 3D mesostructured...
III-V semiconductor photonic crystal by using a hydride vapor phase epitaxy technique. The optical properties of the epitaxial GaInP as photonic crystal matched the simulation results indicating complete filling of the template. Importantly, the nature of the epitaxy and the texture of 3D GaInP were preserved during the growth through the complex geometry of the template as confirmed by X-ray diffraction and high resolution transmission electron microscopy. XRD reciprocal space mapping of the epitaxial layer grown through the 3D template demonstrates that the film is nearly fully relaxed with a negligible strain gradient and a main strain relaxation source appears to be stacking faults and dislocations rather than composition variations. Controllable optical properties should be expected for this HVPE technique based fabrication of optoelectronic device with the freedom in both the photonic crystal geometry and the GaInP composition. This work extends the scope of the very few known methods\(^1\)\(^–\)\(^3\) for the epitaxial fabrication of 3D mesostructured solids to the well-developed HVPE technique. Such approach may be applicable for the fabrication of a range of structured materials for functional optoelectronics, photocatalysis, and thermoelectric with the required low defect densities and tunable characteristic mesostructured dimensions.

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