Epitaxial growth of three-dimensionally architectured optoelectronic devices

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Figure S1. Electrical characteristics of a series of 3D structured devices. a, A series of I-V curves are shown for an array of devices (inset). The diameter of each device is 120µm. b, Plan view and c, angle view close-up SEM of a 3D structure LED. The rough surface around the device is due to the non-uniform etch rate during ICP-RIE caused by the porous structure.
Figure S2. Light emission versus current behavior of 3D photonic crystal LEDs. The light output as a function of current running through the LED is plotted (red line is a linear fit to the data). The corresponding IR camera images are shown to the right of the plot.

Selective Area Epitaxy

Traditional 2D selective area epitaxy relies on a strong preference for growth on the semiconductor substrate rather than the mask material\textsuperscript{1-4}. It has been shown previously that the nucleation behavior on the mask is strongly affected by the partial pressure of the precursors over the mask surface where nucleation does not occur below a certain threshold. Finite element modeling of the concentration profile over the 3D mask was performed following previously published procedures\textsuperscript{3,5}. Diffusion through the 3D mask was modeled using Knudsen and Enskog diffusion\textsuperscript{6}, allowing calculation of the partial pressure above the mask for each thickness in Figures 3c-e (Fig. 3f, red circles). The threshold partial pressure for nucleation in this template is expected to be approximately the partial pressure over the mask in Figure 3e where nucleation did not occur. The reactor conditions may be designed such that the partial pressure over the thick regions may be maintained below the nucleation threshold (Fig. 3f, black circles), resulting in nucleation-free mask surfaces (Fig. 1a) and, thus, epitaxial films. The control over the group III source partial pressure is achieved by controlling the reactor pressure and inlet partial pressure (flow rate) of the source. In addition, the temperature has a strong effect on the nucleation behavior due to reduction in diffusion constant and variation in sticking coefficient. The reactor pressure may also affect the decomposition behavior and sticking coefficients of precursors, improving the selectivity of growth\textsuperscript{5,7}, thus reactor pressure was kept low, at 50mBar.

Pole figure measurements of a 3D photonic crystal sample (Fig. 2b) demonstrate that the sample does have an epitaxial relationship to the substrate, however a number of peaks are seen in addition to the \{220\} family of planes. These peaks may be explained by (111) twinning, which is often observed in synthesis of III-V nanostructures. The angle between \{004\} and the \{220\} family of planes is shown in Supplementary Table S1 along with the angle of the \{228\} family of planes which are the resultant orientation of \{220\} after twinning about \{111\}. Analysis of the pole figure
some threshold partial pressure\(^5\). Finite element modeling of the concentration profile
over the 3D mask was performed following previously published procedures\(^3,5\). Diffusion
through the 3D mask was modeled using Knudsen and Enskog diffusion\(^6\), allowing
calculation of the partial pressure above the mask for each thickness in Figures 3c-e (Fig.
3f, red circles). The threshold partial pressure for nucleation in this template is expected
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Pole figure measurements of a 3D photonic crystal sample (Fig. 2b) demonstrate
that the sample does in fact have an epitaxial relationship to the substrate, however a
number of peaks are seen in addition to the \{220\} family of planes. These peaks may be
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nanostructures. The angle between \{004\} and the \{220\} family of planes is shown in
Supplementary Table S1 along with the angle of the \{228\} family of planes which are the
resultant orientation of \{220\} after twinning about \{111\}. Analysis of the pole figure
(Fig. 2b) shows that the 19.47° and 76.37° peaks are present. The additional planes may be explained by a second twinning of the previously twinned planes.

<table>
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<tr>
<th>Conversion for (111) Twinning</th>
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<td>Initial Angle</td>
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<td>{220}</td>
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Table S1. Conversion for (111) twinning. Angle of planes relative to (004) both before and after twinning about (111) planes.

Surface Passivation of 3D Structures

The unoccupied bonds at the surface of a III-V device may act as carrier traps, resulting in non-radiative recombination and significant degradation of device performance and efficiency. It is therefore essential to have control over surface recombination for any practical III-V device. This is typically achieved by passivation of the dangling bonds on the exposed surface of the material, commonly by growing a wider band gap semiconductor by epitaxy. We demonstrate surface passivation using a GaAs/AlGaAs/GaAs growth step after template inversion. The passivation layer shows significant faceting of the surface after growth (Fig. 4c) as compared to the initial structure (Fig. 4b) which is indicative of the epitaxial growth process. Photoluminescence measurements, used to investigate the effectiveness of the passivation process, were performed on multilayer structures (Supplementary Figs. S3b, c) which are comparable in surface area and geometry to the devices shown in Figure 5. Studies of the passivation effectiveness of samples with heterostructures were also performed. Optimization of the preparation conditions before growth of the passivation layer, specifically an ammonia-
based oxide etch performed in a nitrogen atmosphere with no subsequent exposure to oxygen before growth, resulted in an increase in PL intensity of 20 times (Supplementary Fig. S3a).

Figure S3. Passivation of multilayer 3D structured materials. a, Photoluminescence spectra of a GaAs 3D structured material containing an InGaAs layer 200nm below the upper surface. Spectra are shown before (red) and after (black) growth of a 10nm GaA/AlGaAs/GaAs passivation layer on the surface. b, Plan view and c, cross-section scanning electron micrographs of a multilayer 3D structure. The cross-section image shows a two layer structure; the second layer has been lost at the edge of the sample due to cleavage of the wafer.

Electroluminescence From 3D Photonic Crystal LEDs

The 3D photonic crystal LEDs are quite stable under measurement conditions and only tend to fail at high drive currents. The LED failure mechanism appears to occur through one of two pathways. In one case thermal damage occurs near the probe/contact...
interface, observed as a flash on the IR camera image. Visible light images show a darkened region on the contact where the damage occurs. The onset of the other failure mode is gradual with regions of the LED dimming stochastically until, eventually, there is no emission. Perhaps the 3D network is breaking due to resistive heating in the narrowest regions. However, if the LED was not driven at high current where the gradual failure occurs levels (> 12mA for typical device used in this work), the output remained constant for the duration of the measurement (10 minutes).

Electroluminescence from two 3D photonic crystal (PhC) LEDs are shown in Figure 5f. The 3D PhC LEDs have different lattice constants (a=1035nm and a=735nm) but similar emission wavelengths, therefore the interaction between the emitted light and the 3D structure is expected to be different for the two structures and may be analyzed by comparison to photonic band structure calculations Band structure calculations assume an infinite periodic structure; however, experimentally, this is not the case. When a photonic crystal is thin (<10 layers) deviation from band structure will likely occur\(^8\), namely smearing out of fine features such as narrow band gaps, making it difficult to infer detailed information about the PhC behavior by comparison to band structure calculations. However, while detailed information may be lost, more general characteristics may be studied.

The band structure calculations and electroluminescence spectra of the two LEDs before and after infiltration of a solvent (o-xylene or dodecane) are shown in Supplementary Figure S3. The emission from the 3D PhC LED with smaller lattice constant (Supplementary Fig. S4, black curves) appears unmodified by the photonic crystal owing to the fact that the emission wavelength is at a relatively low energy
(a/λ=0.6) and lies almost entirely outside the large pPBG a/λ=0.48. The larger lattice constant 3D PhC LED (Supplementary Fig. S4, red curves) however displays a distinct change in spectral shape upon infiltration of o-Xylene. Based on comparison to the spectral shape of the unmodified emission (a=735nm, Supplementary Fig. S4, black curves) it appears that the GaAs/air structure is modifying the emission of the a=1030nm LED (Supplementary Figure S4a, red curves) by increasing the emission intensity from a/λ=0.97 to 1.04, and possibly suppressing the emission from a/λ=0.8. Infiltration of solvent appears to negate this enhancement/suppression as the spectral shape of the EL after infiltration of o-Xylene (Supplementary Fig. S4c) is quite similar to the unmodified EL spectra (a=735nm, Supplementary Figure S4, black curves).

We suspect the series of flat bands in the a/λ=0.97 to 1.04 range are resulting in an increase in the optical density-of-states (DOS) and thus an increase in the emission from the InGaAs according to Fermi’s golden rule. Infiltration of solvent results in increased curvature of the bands in this energy range and likely a reduction of this DOS enhancement. The band gap at a/λ=0.8 is possibly suppressing emission in this energy region for the GaAs/air structure. In addition, the narrow pseudo photonic band gaps at a/λ=0.97 and 1.02 are likely closed due to the finite thickness of the structure, which is why suppression is not observed in this energy range.
Figure S4. Comparison of band structure calculation and electroluminescence of 3D PhC LEDs. 

**a**, Band structure calculation of a GaAs/air 3D photonic crystal. The electroluminescence spectra of two 3D PhC LEDs is plotted on the band structure for lattice constants a=1030nm (red) and a=735nm (black). **b**, Band structure calculation of an o-xylene infilled GaAs 3D photonic crystal. The electroluminescence of a 3D PhC LED (a=1030nm) infiltrated with o-Xylene is shown. **c**, Band structure calculation of a dodecane infilled GaAs 3D photonic crystal. The electroluminescence of a 3D PhC LED (a=735nm) infiltrated with dodecane is shown.
References


