Supplementary information

Structural characterization

The fabricated p-type single crystal diamond membranes were characterized using Raman spectroscopy. The diamond membrane were probed with a 633 nm HeNe laser and a peak at ~1332 cm⁻¹ corresponding to a single crystal diamond is shown in Figure S1(a) with a full width at half maximum (FWHM) of 8.3 cm⁻¹⁵⁰. The FWHM is broader than a standard undoped diamond, but in accord with the boron doped diamonds⁵⁰.

To measure the surface roughness, the membranes were scanned using an atomic force microscopy (AFM) immediately after lift-off, post thinning processing and after regrowth. The scans are shown in figure S1(b). As expected the overall surface roughness is maintained. The surface roughness is estimated to be below 3 nm, and the data is shown in figure S1(b).



Figure S1. Structural characterization. (a) Raman spectroscopy of the p-type diamond membrane using a 633 HeNe laser shows the characteristic single crystal diamond peak at 1332 cm⁻¹. The curve was fit with a Voight function to show a FWHM of 8.3 cm⁻¹. (b) Lateral AFM scan show the surface roughness of the membrane after lift-off, after thinning and after an overgrowth to be ~2.5 nm, ~1.5 nm and ~ 1.5 nm respectively. (c) TEM image of an overgrown diamond membrane (~250 nm in thickness) transferred to a copper TEM grid. Inset: higher magnification image of edge region. Scale bar 20 nm. (d) Diffraction pattern from the diamond membrane in (c) indexed to the [001] zone axis.

To unambiguously show that we overgrow a single crystal diamond, the overgrowth membranes are transferred to a TEM grid. The typical membrane morphology after etching and epitaxial overgrowth is shown in the TEM micrographs in Figure S1c. Select-area electron diffraction confirms the membrane microstructure is a single crystal (Figure S1d). The diffraction intensity pattern is indexed

to the [001] zone axis of a diamond cubic structure. The measured plane spacing of (200) and (220) planes were 1.275 and 0.903 Å respectively, in good agreement with bulk diamond. TEM and SAED characterisation were conducted on a FEI Tecnai T20 microscope at 200keV with a LaB 6 filament. The overgrown n-type layer was proved using a secondary ion mass spectrometry (SIMS) measurement, to quantify the phosphorus concentration (figure S2). The measurement was done on an epitaxial layer that was grown under identical conditions for a longer time. The doping concentration was determined to be $\sim 1 \times 10^{18}$ atoms/cm² (blue curve). The red curve represents the detection limit of the boron atoms.



Figure S2. SIMS analysis. Secondary ion mass spectrometry measurement of CVD grown phosphorus doped diamond. Hydrogen, nitrogen and boron exhibit background noise while Phosphor shows a doping concentration of $\sim 10^{18}$ atoms/cm²(blue curve) while the boron shows background noise (red curve.)

Electrical characterization of the devices

Figure S3 shows the same data as in figure 3 (e, f) through a semi log I-V curve showing rectification ratios of $\sim 10^5$ and 30 for the 1.9 µm and 300 nm membrane, respectively. The reduction in rectification efficiency may be due the non-homogeneous boron doping near the diamond surface.



Figure S3. Log (I) vs (V) rectification curves of (a) 1.9 μ m p-n diamond membrane after electrochemical etching, showing a high recitation of ~18300 and (b) a thinned ~ 300 nm p-n

membrane showing a rectification ratio of \sim 30. The ratio was determined by dividing the value at which the current plateaus at an identical forward and reverse bias.

We also realized a hybrid optoelectronic device, whereby the p-type membrane is overgrown with intrinsic single crystal diamond containing silicon vacancy (SiV) defects. An optical image of the overgrown membrane containing silicon vacancy (SiV) color centers is shown in figure S4a and the optical properties of the membrane are shown in figure S4b, confirming the presence of strong SiV luminescence centered at 737 nm. The overall thickness of the SiV containing membrane is ~ 300 nm. To study the electrical properties of these membranes, we sputter ~100 nm of n-doped ITO through a defined lithography mask to create the final p-i(Diamond) – n-type(ITO) junction (figure S4c). Figure S4d shows the I-V characteristics, with diode-like behaviour and a threshold voltage of ~ 10 V. A semi log IV curve of the hybrid device, shows a rectification ratio of 3×10^3 . Such hybrid devices can be interesting to explore in conjunction with other semiconductors such as ZnO which exhibits excellent n-type characteristics for creating of efficient LEDs and heterojunctions.



Figure S4. (a) An optical image of the overgrown membrane (200 nm p-type base with 100 nm of intrinsic layer with SiV centres). (b) Photoluminescence measurements recorded at room temperature showing a characteristic emission from the SiV centers at ~737 nm. (c) Schematic diagram of the hybrid diamond/ITO device. (d) The p-i-ITO membrane is semiconducting with an on-set voltage of ~ 10V.Inset: Log (I) vs (V) rectification curves of a p-i-ITO diamond membrane showing a recitation ratio of ~3000.

Band diagram and recombination model

Figure S5 shows the band diagram of a typical all diamond p-i-n junction. W_{Ti} corresponds to the work function of titanium, E_F and E_{EF} are the fermi and effective fermi level after doping, respectively. V_O is the step in energy between the bands of the p and n doped diamond regions. The boron and phosphor

energy levels were taken as 0.36 and 0.57 eV, respectively. E_{FIP} and E_{FIN} are the effective fermi energies for the p doped and n doped diamond layers.

The Langevin recombination model considers the Coulomb interaction process to capture the carriers within a selected device. The model is typically applied for materials with low mobility ^{1, 2}. The recombination rate, U_{Lan} , in the Langevin model is given by

$$U_{Lan} = \frac{\pi r_c^2 J}{q}$$

where J is the current density and q is the charge of an electron. The Coulomb capture radius, r_c , is given by

$$r_c = \frac{q^2}{4\pi\varepsilon_r\varepsilon_0 kT}$$

where ε_r is relative permittivity, ε_0 is the vacuum permittivity, k is the Boltzmann's constant and T is temperature in K.

In diamond, \mathcal{E}_r is approximately 5.7. Therefore, r_c is predicted to be approximately 9.7 nm at room temperature (300 K). The current density for our devices, J, at ~2 mA is estimated to be 3×10^4 A/m² for a ~800 µm x 200 µm diamond p-n membrane. Accordingly, U_{Lan} is calculated to be 5.6×10^7 s⁻¹ corresponding to pumping rate of ~ 20 ns. This rate is slower than the spontaneous emission rate of the SiV, that may explain the lower EL signal.

The Langevin model is valid if $\lambda_m \ll r_c$ [1]. The mean free path, λ_m , can be written as

$$\lambda_m = \frac{\mu (3kTm^*)^{\frac{1}{2}}}{q}$$

where μ is mobility, $m^* = 0.8m_e$ and $\mu = 100 \text{ cm}^2/Vs_{,} \lambda_m$ is approximated to be ~5.8 nm, which is indeed lower than r_c .



Figure S5. Band diagram of the p-i-n diamond device. (a) Diagram illustrating when Titanium (Ti) comes into contact with the n-layer of the diamond membrane. E_{EF} is the effective fermi level, E_F is the fermi level and W_{Ti} is the work function of Ti. (b) Band diagram of the p-i-n diamond membrane at equilibrium. The boron and phosphor energy levels were taken as 0.36 and 0.57 eV respectively.

References

- 1. Pope, M. Swenberg, C. Electronic Processes in Organic Crystals and Polymers, (Oxford Univ. Press, 1999).
- 2. Mizuochi, N, Makino, T, Kato, H, Takeuchi, D, Ogura, M, Okushi, H, Nothaft, M, Neumann, P, Gali, A, Jelezko, F, Wrachtrup, J, Yamasaki, S, "Electrically driven single-photon source at room temperature in diamond", Nature Photonics, Vol 6, 2012.