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Highly oriented, free-standing, superconducting NbN films growth on chemical vapor deposited graphene

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NbN films are grown on chemical vapor deposited graphene using dc magnetron sputtering. The orientation and transition temperature of the deposited films is studied as a function of substrate temperature. A superconducting transition temperature of 14 K is obtained for highly oriented (111) films grown at substrate temperature of 150 °C, which is comparable to epitaxial films grown on MgO and sapphire substrates. These films show a considerably high upper critical field of ∼33 T. In addition, we demonstrate a process for obtaining flexible, free-standing NbN films by delaminating graphene from the substrate using a simple wet etching technique. These free-standing NbN layers can be transferred to any substrate, potentially enabling a range of novel superconducting thin-film applications. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4875356]

There is a resurgence in research on high-quality superconducting thin films as they provide an excellent platform for fabricating hot-electron bolometers (HEB) for terahertz detection and single-photon detectors with high speed operation and low dark counts, enabling applications in quantum optics.1 Much of the work on superconducting single photon detectors (SSPD) has been based on NbN thin films,2-4 since NbN has a relatively high superconducting transition temperature, $T_C \sim 16$ K, and a short superconducting coherence length of a few nanometers and fast energy relaxation time. For increased detector efficiency by integrating SSPD with optical structures, NbN growth on non-conventional substrates like GaAs,5,6 3C-SiC,7 and Si8 has been explored. Increased efficiency of terahertz detection is achieved by thermal isolation of HEBs by depositing NbN films on air bridges formed by thin membrane of Si$_3$N$_4$,9 to improve the quality of these films alternative materials for buffer layer are being explored.10 Recently there are attempts to transfer the SSPD fabricated on Si$_3$N$_4$ membranes to photonic structures on a secondary chip.11 On-chip graphene-based photo-detectors are another area of research due to simpler CMOS-compatible fabrication techniques.12 Superconductor-graphene hybrid structures have been of recent interest due to tunable superconductivity.13,14 Graphene provides an interesting choice of substrate for superconducting thin films as the low intrinsic carrier density in the graphene reduces the effect of inverse proximity effect from the substrate. Superconducting NbN leads have been used to contact graphene microbolometers for THz detection.15 Here we report the growth and characterization of highly oriented NbN thin films with $T_C \sim 14$ K on large-area chemical vapor deposited (CVD) graphene. Growth on graphene layers transferred onto Si$_3$N$_4$-coated silicon wafers provides an easy route for delamination16 of the graphene layer along with the deposited film. This enables the release of the NbN film from the substrate, thus allowing flexible, free-standing NbN layers to be obtained. These can be transferred to any other substrate, thus providing a simple route for integration with photonic crystals and also an alternative to NbN grown on Si$_3$N$_4$/SiO$_2$ membranes10 for use in HEB.

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Graphene layers were deposited by the standard process of CVD of carbon via the decomposition of methane onto copper foils, specific details of our growth and transfer process can be found in earlier reports. Continuous graphene films with monolayer to few-layer coverage were obtained and transferred onto thermally oxidized silicon wafers with a 300 nm SiO2 layer. Key process steps and Raman spectra of our graphene layers are shown in Sec. I of the supplementary material.

Superconducting thin films of NbN were deposited by low-pressure reactive DC magnetron sputtering on these CVD graphene layers. The conditions for deposition were chosen based on earlier experiments on the optimization of the growth of epitaxial NbN films on MgO which resulted in films with a $T_c$ of $\approx 16$ K. A Nb target was sputtered at a power of 230 W in a mixture of Argon and Nitrogen (Ar:N2::80:20) at an ambient pressure of 4.8 mTorr ($6.4 \times 10^{-6}$ bar). For the first set, while the sputtering power, gas pressure and gas ratio were kept constant, the substrate temperature ($T_{sb}$) was varied from room temperature to 600 $^\circ$C and the sputtering was carried out for 3 min. In the second set, the temperature was kept constant at 150 $^\circ$C and the time of deposition varied from 7 s to 3 min resulting in films in thickness ranging from $\sim 10$ nm to 250 nm. Section II of the supplementary material discusses the morphology and electrical characteristics of films deposited for very short times (3 s and 5 s). The 3 s film was discontinuous and insulating. Reproducible values of $T_c$ were obtained only for films grown for 7 s or longer. The structural and electrical properties of these films are discussed next.

Figure 1(a) shows the x-ray diffraction profile ($2\theta$ scan) for $\sim 250$ nm thick NbN films grown at different substrate temperatures ($T_{sb}$). For films grown at temperatures ranging from $30^\circ$C to $450^\circ$C, peaks corresponding to (111) and (200) cubic $\delta$-NbN can be seen. Additional peaks for...
TABLE I. Superconducting transition temperature and width of transition of NbN films deposited at various substrate temperatures.

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>$T_C$ (at 10% $R_N$)</th>
<th>$\Delta T_C$ (10%–90% of $R_N$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 $^\circ$C</td>
<td>13.1 K</td>
<td>0.13 K</td>
</tr>
<tr>
<td>150 $^\circ$C</td>
<td>14.11 K</td>
<td>0.14 K</td>
</tr>
<tr>
<td>300 $^\circ$C</td>
<td>13.94 K</td>
<td>0.39 K</td>
</tr>
<tr>
<td>450 $^\circ$C</td>
<td>14.2 K</td>
<td>0.37 K</td>
</tr>
<tr>
<td>600 $^\circ$C</td>
<td>13.7 K</td>
<td>0.6 K</td>
</tr>
</tbody>
</table>

hexagonal $\epsilon$-NbN are observed in film grown at 600 $^\circ$C. Based on the ratio of the heights of the peaks corresponding to diffraction from the (111) and (200) planes, the film grown at 150 $^\circ$C can be identified as the most oriented film along the (111) direction. Figure 1(b) shows the variation of the superconducting critical temperature with $T_{sb}$. The transition temperature is taken to be the temperature at which resistance reached 10% of the normal state value. The superconducting transition width ($\Delta T_C$) is defined as the temperature range between which the resistance is at 10% and 90% of the normal state value. In these samples, $\Delta T_C$ increases for deposition temperatures above 150 $^\circ$C, which is due to existence of different orientation of crystallites as evident from the decreasing ratio of (111) and (200) peaks in the x-ray diffraction profiles. $T_C$ and $\Delta T_C$ are tabulated in Table I for various substrate temperatures.

The morphology of all the films remains similar with triangular grains with a nominal increase in grain size with $T_{sb}$. Figure 2(a) shows an SEM micrograph of a film grown at 150 $^\circ$C. Raman spectroscopy mapping at room temperature on the same sample (inset of Figure 2(b) shows complete coverage of NbN on graphene over the 20 $\mu$m $\times$ 20 $\mu$m scan region. The point spectrum in Figure 2(b) shows the typical broad NbN Raman feature as well as the characteristic signatures of the 520 cm$^{-1}$ peak from the silicon substrate and the G, D, and 2D peaks arising from the graphene layer. The presence of the peaks from the underlying graphene layer indicates that the thin layer indeed survives the plasma ambient during the sputtering process.

Since the films deposited at 150 $^\circ$C are the most oriented with a sharp superconducting transition, we chose this as the substrate temperature for further investigation of the properties of samples of different thickness.

The Ginzburg Landau coherence length ($\xi_{GL}$) is estimated from the temperature dependence of the upper critical field ($H_{c2}$) for a ~250 nm film. Figure 3 shows a series of resistance vs. temperature curves as a function of applied field from 0 T to 8 T. The inset plots the upper critical field as a function of the transition temperature. We estimate $H_{c2}(0)$ and $\xi_{GL}$ using the dirty limit relation:

$$H_{c2}(0) = 0.69 T_C \frac{dH_{c2}}{dT} \bigg|_{T=T_C}$$

and

$$\xi_{GL} = \left[ \frac{\phi_0}{2\pi H_{c2}(0)} \right]^{1/2}.$$
FIG. 3. Resistance as a function of temperature for a 250 nm thick NbN film grown at 150°C under different applied magnetic fields. The successive plots are for magnetic fields of 0, 1, 2, 3, 4, 5, 6, 7, and 8 T. Inset shows the upper critical field as a function of transition temperature in presence of a magnetic field for the same film.

FIG. 4. Normalized resistance as a function of temperature for films with different thickness obtained by varying the deposition time. Transition temperature decreases monotonically with thickness of films.

From our data, the value of $H_{c2}(0)$ is estimated to be 33.6 T and $\xi_{GL}$ is $\sim$3 nm, respectively. This value of the upper critical field for NbN grown on CVD graphene is considerably larger than the 20 T reported on NbN films grown of MgO with similar transition temperature and suggests that the NbN/graphene films can be useful for high magnetic field applications.

Figure 4 shows the resistance vs. temperature curves for films deposited for different times which correspond to different film thicknesses ranging from 10 nm to 250 nm. The film thickness was estimated from deposition time and cross-sectional SEM. On reducing the thickness of films, there is a monotonic decrease in transition temperature. The effect of disorder becomes more pronounced at lower thickness leading to localization of electrons which results in reduced screening thereby lowering the transition temperature.

Since the NbN/graphene films are on oxidized silicon substrates, free standing NbN films can easily be obtained by using the underlying SiO$_2$ as a sacrificial layer. Graphene is not attacked by HF and etching SiO$_2$ below the graphene layer has been a standard route for fabricating suspended graphene devices. In our process, we first spin-coat the NbN film with $\sim$300 nm of poly(methyl...
methacrylate) (PMMA) for protection. Then the edges of the film are scratched to expose the SiO$_2$ layer underneath, and the sample soaked in buffered HF solution (concentration: HF:NH$_4$F::1:7). Once the sacrificial SiO$_2$ layer is etched away, the NbN/graphene layer covered with PMMA floats to the top of the solution. The process takes approximately 30 min for a 1 cm$^2$ film. This floating film is then scooped on a glass slide or any other target substrate. The protective PMMA layer is removed using a cycle of rapid thermal annealing (RTA) (300 °C for 10 min and 350 °C for 5 min in 100 sccm Ar). The graphene layer can be removed by oxygen plasma etching if necessary.

Figure 5 shows the normalized resistance vs. temperature curves for the NbN/graphene film before and after delamination from the SiO$_2$/Si substrate. The inset shows the floating PMMA/NbN/graphene film after the SiO$_2$ has been etched away. There is only a very slight decrease in transition temperature which indicates the robustness of this technique.

The use of large-area CVD graphene offers a promising alternative to conventional substrates for the growth of NbN. We have shown that (111)-oriented NbN films with $\sim$14 K transition temperature and very high upper critical field (33 T) can be obtained via growth on graphene layers. The additional advantage of the process is that free-standing, flexible NbN films can easily be obtained, which could enable new designs for HEB and SSPD devices. In combinations with CMOS compatible fabrication of graphene, this opens up a possibility for direct on-chip integration of NbN for superconducting thin-film devices.

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13 A. Allain, A. Han, and V. Bouchiat, Nat. Mater. 11, 590 (2012).
20 See supplementary material at http://dx.doi.org/10.1063/1.4875356 for additional details of graphene growth and NbN growth at low coverage and on different substrates.