Covalent Diamond–Graphite Bonding: Mechanism of Catalytic Transformation

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ABSTRACT: Aberration-corrected transmission electron microscopy of the atomic structure of diamond–graphite interface after Ni-induced catalytic transformation reveals graphitic planes bound covalently to the diamond in the upright orientation. The covalent attachment, together with a significant volume expansion of graphite transformed from diamond, gives rise to uniaxial stress that is released through plastic deformation. We propose a comprehensive model explaining the Ni-mediated transformation of diamond to graphite and covalent bonding at the interface as well as the mechanism of relaxation of uniaxial stress. We also explain the mechanism of electrical transport through the graphitized surface of diamond. The result may thus provide a foundation for the catalytically driven formation of graphene–diamond nanodevices.

KEYWORDS: diamond-to-graphite transformation, Ni-catalyzed graphitization, diamond–graphite covalent bonding, atomically resolved TEM, electrical conductance, plastic deformation

The magic of carbon as an element lies in its ability to hybridize the electronic orbitals in diverse configurations. Thereby, carbon can form covalent structures in one dimension (carbyne), two dimensions (graphene), and three dimensions (diamond). Importantly, the diamond and graphene crystals differ in their electronic structure: the electronic energy band gap of ~5.5 eV for diamond versus the 0 eV band gap of graphite raises interest for various applications. Placing graphene on a diamond surface can result in electronic devices exhibiting superior performance due to nonexistent electronic contamination in the all-carbon environment. However, the production of such devices remains a challenge.

It has been reported that a direct graphitization of the single-crystal (111) diamond surface at temperatures >1373 K yields several layers of graphite formed parallel to the diamond surface. To reduce the high temperatures of graphitization, the use of metal catalysts has been explored. Ni has been conventionally used as a catalyst in mainstream methods of chemical vapor deposition (CVD) synthesis of graphene and carbon nanotubes. Although the growth mechanism of nanotubes from carbon supplied through gaseous precursors has been described thoroughly, a clear understanding of the catalytic growth mechanism of graphene or graphite from solid carbon sources has not yet been provided. The use of Ni on single-crystal and polycrystalline diamonds often results in a formation of uncontrolled number of graphitic layers at the Ni–diamond interface or on top of the catalyst, impeding the formation of high-quality graphene-on-diamond. On ultrananocrystalline diamond the catalytic reaction leads to a Ni-carbon layer exchange yielding single-layer graphene, however, without preserving the initial diamond. In this paper, we study the atomic structure of diamond–graphite interfaces formed by a Ni-mediated transformation. Using aberration-corrected transmission electron microscopy (TEM) applied to specimens in cross-sectional geometry, our atom-by-atom observation provides important insight into the interaction between two carbon lattices with extremely...
different electronic properties; it explains the process of a nanocrystalline diamond (NCD) to graphite transformation mediated by Ni while drilling channels along grain boundaries. The hemispherical morphology of the protruding Ni nanoparticles as well as the crystal orientation and lattice defects of the graphite are explained in terms of a high uniaxial stress that builds up in the channels due to the volume expansion caused by the allotropic transformation. As a highlight, the experimental results provide strong evidence for covalent bonding of graphite to diamond. Electrical transport through the graphitized surface of diamond is interpreted by a modified fluctuation-assisted tunneling mechanism, showing a possible way for graphene–diamond devices.

RESULTS AND DISCUSSION

Figure 1a shows a scanning electron microscopy (SEM) image of the as-grown NCD film prior to Ni deposition. Faceted crystals (average size of ~250 nm) that are frequently twinned are clearly resolved. Charging under the scanning electron beam causes their contrast to be brighter in the upper left than the lower right. After the deposition of 20 nm Ni layer, the topographic contrast of the diamond grains appears more homogeneous due to an even charge distribution on the conductive surface (Figure 1b). The secondary electron (SE) image of the sample annealed at 1073 K for 10 min (Figure 1c) shows a granular and corrugated surface topography. A high number density of round Ni nanoparticles (~45 particles per square micrometer, average size of ~110 nm) is observed at
Nevertheless, we managed to obtain an excellent edge-on geometry which is often obscured by moiré fringes. A typical HRTEM image (as presented in Figure S2) shows that the interface runs along (111), and the beam direction (BD) is [110]. Therefore, an epitaxic crystallographic orientation relationship holds between the two lattices. The large diamond surface segment parallel to {111} is only a particular case of all possible diamond surface orientations. Nevertheless, it can be considered as a model diamond–graphite interface, as similar interface structures (interfaces segments parallel to low-index planes of diamond and perpendicular to graphite basal planes) are frequently present at the channel walls. The (111) termination plane in diamond imaged in Figure 3a is the most stable orientation and forms an atomically sharp interface with graphite. The (111) diamond planes have an inclination of ∼25.5° with respect to the (0001) graphite planes. Because the image is calibrated by adjusting the interplanar spacing of the (111) diamond planes to 0.206 nm (see ref 18), an average interplanar distance of the (0001) graphite planes of 0.359 nm is obtained. This is higher than the interplanar distance of 0.334 nm (see ref 19) for AB- and ABC-stacked graphite but only slightly differs from the distance of 0.355 nm (see ref 20) reported for the AA-stacking. The stacking sequence is confirmed by analyzing the projected atomic columns of graphite in the Fourier-filtered image (see Figure 3b, taken from the area marked by the dashed rectangle in Figure 3a using a slightly different defocus). Considering the angle between these layers and the interface (∼84° and 70.5°, respectively), the projected distance at the interface yields a

Figure 3. Diamond–graphite interface. (a) HRTEM image of the diamond–graphite interface (BD = [110] = [1120]). (b) Fourier-filtered image of the area marked by a yellow rectangle in (a). The filtered image is superimposed by a structural model of the interface where graphitic (0001) planes in an AA-stacking sequence are attached to the (111) surface of diamond. In the structural model directly at the interface, terminating atoms show a tendency to relax to minimize bond length. In particular, the second (0001) graphite plane from the right has two possibilities for relaxation (either relaxing to the left, see the bright atoms, or right).
ratio of 1.65, which deviates quite considerably from a proposed coherent lattice match (ratio of 1.5), where at an \{112\} interface of diamond, 3 \{111\} planes merge to two (0001) graphite planes.\(^2\)

The Fourier-filtered image of the area marked with the white dashed rectangle from Figure 3a was further analyzed in Figure 4a,b, where we plotted the intensity profiles of the first four atomic planes parallel to the interface for diamond along the [121] direction and for graphite along \sim\{0001\} direction. With increasing distance from the interface, the planes are labeled with \(i = 1, 2, 3, \ldots\) in diamond and \(i = -1, -2, -3, \ldots\) in graphite. There is no regular match of the projected atomic columns between the planes 1 and \(-1\) at the interface. In addition, coherency dislocations are absent. To create coherent diamond–graphite interfaces, a number of solutions were proposed in literature, but none of them can be applied to our results. Stacking faults in the diamond proposed to create a coherent interface were not observed;\(^3\) neither the three \{111\} to two (0001) planes (3 to 2)\(^2\) nor a 2-to-1 conversion of these planes were observed.\(^4\) Our experimental result identifies an incoherent interface between diamond and graphite. To evaluate the type of bonding at the incoherent interface, we measure the distances of the adjacent (111) planes \(i\) and \(i+1\), and (1100) planes \(i\) and \(-i-1\) running parallel to the interface and plot in Figure 4c. While the interplanar distances in diamond are in good agreement with the literature value 0.206 nm (see ref 18), the distances in graphite are slightly lower than those calculated from the reported value 0.213 nm (see ref 20) (horizontal dashed lines in Figure 4c). The interface width between the diamond plane 1 and graphite plane \(-1\) (labeled as 0) is 0.223 nm, which is only slightly larger than the values for the covalently bonded planes (111) of diamond and (1100) of graphite (\sim 8% and 5%, respectively). This indicates a similar covalent nature of bonding between the terminating diamond and graphite atoms at the interface. This raises the question of whether or not covalent bonds across an incoherent interface are possible. Based on the results of first principal calculations outlined in refs 22–24), covalent bonds were found across incoherent interfaces. However, this is very depending on the local relaxed atomic configuration. In particular, the formation of covalent bonds is favored when the terminating atoms on both sides of the interface are located atop of each other (i.e., with a minimal distance). In our experimental result, the HRTEM contrast distant from the interface is well-matched by rigid structural models of diamond and graphite (in Figure 3b, the structural model is superimposed on the bright dots, assuming that they correspond to the position of the projected atomic columns). Directly at the interface, the terminating atoms of graphite were allowed to deviate from the rigid structural model to match the HRTEM contrast best. Interestingly, the relaxed positions all show a tendency of adopting short-distance on-top configurations with the terminating atoms of diamond. This is exactly what is predicted theoretically for the formation of covalent bonds (see refs 22–24). In Figure 3b, even strong evidence of splitting of atomic positions of graphite is obtained when the termination is approximately in the middle of two terminating diamond positions (see the second atomic column of graphite from the right). To achieve on-top positions, part of the graphite atoms in the projected atomic column seem to move to the left and part to the right.

The covalent bonding restricts the terminating atoms of graphite to a close distance from the terminating (111) plane of diamond, which, in turn, imposes the AA-stacking sequence
of the (0001) graphite planes to form near the interface. However, the HRTEM images projecting atomic columns of the (0001) graphite provide evidence that, in the center of graphitic channel, the atomic configuration adopts the AB-stacking sequence, i.e., its low-energy structural modification; Figure S5 presents one of the regions with AB-stacked layers. Using the intensity profiles of Figure 4b, the distances of adjacent atomic columns along the interface were measured. Figure 4d shows the standard deviation (SD) of these interatomic distances in the diamond (111) and graphite (1100) planes. Starting from the interface, the SD decreases rapidly on both sides of the interface (more rapidly for diamond than for graphite) and saturates below a value ~15 pm after four layers. However, a significant increase of SD by a factor of ~3 for the interfacial layers indicates local rearrangements of atoms to optimize covalent bonding across the interface.

There is further indication of a strong covalent bond at the interface. Figure 5 shows a channel filled with graphite, where the (0001) planes are clearly resolved. We observe a dependence of the orientation of these lattice planes on the position along the channel. Starting from the dashed line where the graphite planes are flat, they increasingly bend with increasing distance along the z-axis of the channel (Figure 5).

The panels 1–3 in Figure 5 show fast Fourier transform (FFT) representations (displayed as the power spectra) of the graphitic structures inside the squares 1–3 at the lower right wall of the channel in NCD displayed in the TEM image. Overall, the orientation of graphitic planes in the channel can be well described with circular segments (Figure 5 and the sketch in Figure 6a). The curvature (inverse of the radius) of the circular segments as a function of the distance from the Ni particle is shown in Figure 6b (negative and positive values correspond to a concave and convex curvature, respectively). While the basal planes attached to the Ni particle exactly follow
the slightly concave curvature of the particle backside, the value of the curvature increases with increasing distance along the channel; at a distance of about 30 nm, the curvature is almost zero and then becomes convex. Due to the curvature, the local orientation of graphite at the channel walls also systematically changes with position. The orientation at three different positions along the channel wall (squares 1–3) are analyzed through the FFT (panels 1–3 in Figure S) as follows: arc-like intensity maxima originate from the (0001) planes of the graphite. With the increasing distance from the Ni surface (i.e., from panel 1–3), the averaged rotational orientation of intensity maxima (full straight lines) turns clockwise, accompanied by widening of these segments (dashed lines). Thus, the (0001) planes that are running almost normal to the diamond–graphite interface in position 1 gradually rotate toward the interface with increasing distance from the Ni particle. The widening of the arc-like intensities with increasing distance is related, first, to the increase of the curvature of the (0001) lattice planes and also to the local structural disorder (rotational misorientation of small segments of the (0001) planes), which gradually increases toward the top of the channel.

Quantitatively, the experimental data points are rather well fitted by a simplified model with a single parameter \( \alpha \) that reflects the ratio of the number of lattice planes \( N_c \) formed in the center to those formed directly at the walls, \( N_w \). Therefore, \( (N_c = a N_w) \), which also implies that \( (h + x) = \alpha x \) or \( h = (\alpha - 1)x \), where \( h(x) \) is the height of the circular segment depending on \( x \), the distance from the flat plane assigned to position 0 in Figure 6a. Then the fit to the experimental data of the curvature \( C \) of the graphitic planes (Figure S) is plotted as a function of the distance \( x \) (Figure 6b). Fitting yields a factor of \( \alpha \approx 1.3 \), meaning that about 30% more lattice planes are present in the center than adjacent to the walls of the graphite channel.

However, the geometrical model in Figure 6 does not offer understanding of the mechanism of formation of the graphite-filled channel in NCD drilled by the Ni particle. We propose an explanation of the processes that lead to the formation of the channels along the grain boundaries in NCDs, covalent attachments of graphitic planes to diamond, the curvature of the (0001) basal planes in the channel and the shape the hemispherical Ni particles at the bottom of the channels. Three aspects play a crucial role in these processes: (i) the catalytic reaction of Ni with diamond, (ii) opening dangling bonds on the diamond surface as the Ni particle moves deeper into diamond, and (iii) the volume expansion when diamond transforms to graphite.

In contact with diamond, the Ni particle catalytically releases interfacial carbon atoms. Although the bulk diffusion of C atoms through the Ni particle at temperatures of 1073 K cannot be excluded, studies have shown that the energetically favorable mechanism for the movement of C atoms across a Ni particle is surface diffusion. Therefore, we assume that the carbon atoms released from diamond in front of the propagating Ni particle migrate along the diamond–Ni interface toward the trailing end of the Ni particle; the removal of carbon atoms at the front side of the Ni particle opens space for the Ni particle to penetrate one atomic layer deeper into diamond, leaving behind one atomic layer with dangling bonds at the diamond surface open. The released carbon atoms are available to saturate the dangling bonds of diamond and then to continue to grow a graphene layer along the backside of Ni (Figure S3). This explains the covalent attachment of graphite layers to diamond along the channel walls shown in the TEM image in Figure 3a. Once the first graphene layer has formed, the next layer nucleates due to the constant supply of carbon atoms from diamond at the front of the Ni particle. The length of graphite channels formed during annealing is in the range of 100–150 nm (Figure 2). This is less than that observed in the case of forming free pores by Ni-etching of NCD diamond in a hydrogen atmosphere converting the carbon released from diamond to methane gas rather than to graphite filling the drilled channels as in the present case. A growth rate of graphite in the range of 0.17–0.25 nm/s is obtained (assuming that during annealing at 1073 K for 10 min the Ni particle moved at a constant speed). As shown above, the number of newly formed graphite layers progressively increases from the channel wall toward the center (Figure S). The physical reason for this is a significant increase in the molar volume \( V \) of the forming graphite with respect to that of the removed diamond because, at 1073 K, for graphite, \( V_g = 5.54 \text{ cm}^3/\text{mol} \), and for diamond, \( V_d = 3.44 \text{ cm}^3/\text{mol} \), the ratio \( V_g/V_d = 1.61 \) leads to a uniaxial transformation strain of 0.61 along the z-axis of the channel.

In a confined situation, where the channel is blocked by surrounding diamond crystals, by the Ni particle at the bottom, and by the newly formed graphite at the top, the uniaxial strain is supposed to yield a compressive stress in graphite parallel to the z-axis of the channel. To release this stress, material has to be pushed out of the channel. The covalent bonding of graphite to the channel walls prevents both the upward movement of the graphite column in the channel as a compact block and the migration of material along the channel walls. Considering the crystallographic orientation of graphite with its \( c \)-axis aligned parallel to the z-axis of the channel, a simple estimate based on linear elasticity yields the stress \( \sigma_c = c \varepsilon_c \approx 3.44 \text{ GPa} \), where \( c = 28 \text{ GPa} \) (ref 28) is the elastic constant of graphite at 1073 K, and \( \varepsilon_c \) is the strain in the direction of the \( c \)-axis. Certainly, linear elasticity does not apply for such a large transformation strain. Material must be pushed out of the channel by mechanisms of plasticity, releasing tensile strain to a certain value that can be accommodated elastically. Plastic flow might occur by the glide of prismatic dislocations (with a Burgers vector \( [0001] \) and a glide plane of \( (1120) \) or \( (1100) \)). A large number of isolated dislocations or dislocation dipoles that have a component Burgers vector normal to the basal planes of graphite that equals \( [0001] \) are observed in graphite filling the channel (see Figure S4). In addition, the elastic compressive stress exerted on the graphite channel might also activate other mechanisms of plasticity such as the formation of kink bands, rupture of basal planes, and delamination, which may cause the graphitic layers to pop out of the channel.

Due to the high strain of \( \varepsilon_c \approx 0.61 \), the work \( W = \sigma_c \varepsilon_c \) done by the plastic deformation of graphite, which is necessary to pop material out of the channel, is quite significant (\( \sigma_c \) is the critical stress needed to activate mechanisms of plastic deformation of the graphite). In the literature, an experimental value at room temperature of \( \sigma_c \) in the range of 0.3–0.4 GPa (ref 29) for plasticity of graphite induced by stress acting along the \( c \)-axis (like in the present case) was reported. Using these values yields \( W \) in the range of 1.0–1.4 kJ/mol. This work is provided by the chemical driving force \( \Delta \gamma \) of the transformation (i.e., the difference \( g_c - g_d \) of the Gibbs free enthalpy of diamond and graphite; at the temperature 1073 K, \( \Delta \gamma = -6.3 \text{ kJ/mol} \); see ref 30). Therefore, \( W \) amounts to a fraction of about 20% of the...
chemical driving force. In addition, the residual elastic stress in graphite increases its Gibbs free enthalpy with respect to that of diamond. However, as compared to the total difference of their Gibbs free energies, this increase in elastic energy (given by \((\sigma_0^b)2/2c_{33}\)) is rather moderate (about 0.015 kJ/mol for \(\sigma_0^b = 0.4\) GPa). In other words, the curvature observed in the graphite structure filling the channels edged in NCD is a consequence of a significant uniaxial transformation strain; the corresponding stresses acting along the c-axis of the graphite exceed the critical yield stress to activate mechanisms of plasticity pushing material out of the channel. The work of plastic deformation is provided by the chemical driving force.

As for the shape of the Ni particles, the same reason causing plasticity in graphite above the Ni particle explains their flat backside morphology: the remaining elastic tensile strain in the channel would in turn exert a corresponding compressive stress on the backside surface of the Ni particle. While the surface of the Ni particle in contact with the NCD is rather spherical to minimize the surface area, the backside Ni surface facing graphite is reshaped by the remaining compressive stress and becomes flat or even concave.

Our structural investigations on the atomic scale suggest that the overall structure consists of graphitic domains that might be interconnected into a percolating network. To probe percolation between the domains, characterization on the macroscopic-scale is done by measuring electronic transport along the entire sample surface. The electrical conductance as a function of temperature \(G(T)\) between 4.2 and 300 K measured in the 4-probe configuration is presented in Figure 7a (orange line).

In the case of conductive (graphitic) domains forming a percolating network, the mechanism of electronic transport known as fluctuation-assisted tunneling (FAT)\(^{31-33}\) can be used to describe our system. The FAT model applied to the temperature-dependent conductance curve in Figure 7a fits to our experimental data with an excellent agreement but only when we add a term that is linearly dependent on temperature:

\[
G(T) = G_0T + G_1\exp\left(-\frac{T_b}{T_s + T}\right)
\]

where \(G_0\) is a constant (in units of SK\(^{-1}\)) and \(G_1\) is a prefactor of the residual conductance at \(T = 0\) K, \(T_b\) characterizes the tunneling energy barrier between conductive regions, and \(T_s\) determines tunneling efficiency at \(T = 0\) K. We propose an interpretation of two conductance contributions, where the FAT term with a very small tunneling barrier \((T_b < 2\) K) is assigned to a transport mechanism between graphene flakes within disordered graphitic domains, whereas the linear term corresponds to an “activation” of conduction paths across the boundaries between graphitic domains with irregular distances (see blue and orange arrows in the illustration in Figure 7b).

The full fitting function, as well as each of the terms, are plotted in Figure 7a (as blue dashed lines) and the values of the fitted parameters are \(G_0 = 2.145 \times 10^{-6}\) SK\(^{-1}\), \(G_1 = 0.00246\) S, \(T_b = 1.97\) K, and \(T_s = 9.48\) K. The small value of the tunneling energy barrier of 0.17 meV obtained from the fit corresponds to the charge transport between the graphene flakes in the graphitic domains.

To summarize, we propose a schematic model that illustrates the mechanism of catalytic transformation of the polycrystalline diamond structure into graphite (Figure 8).

- At the contact of Ni particles with diamond, C atoms are catalytically etched preferably at grain boundaries. C atoms diffuse under the Ni surface, propagate along the Ni–diamond interface and are released at the Ni particle back side forming a layer of graphene (Figure 8a). This opens space for the Ni particle to move deeper into diamond. Due to a continuous supply of etched carbon, a second layer of graphene nucleates underneath the first, starting to form a dome of graphite surrounding the particle (Figure 8b,c).
- As the Ni particle moves downward along the diamond grain boundary, a channel is formed, leaving unsaturated dangling bonds at the diamond surface above the Ni particle (Figure 8b,c).
- Free C atoms covalently attach to the dangling bonds of diamond, and graphite grows from the walls toward the center of the channel.
- Significant volume expansion during graphite formation from diamond results in uniaxial stress, released by the mechanism of plasticity that allows graphite to be pushed out of the channel.
- The backside of the Ni particle is flattened by the uniaxial stress of the graphitic planes constrained by the insufficient volume of the channel (Figure 8d).

**CONCLUSIONS**

Our study of the catalytic transformation of diamond to graphite and the obtained results under well-defined experimental conditions enabled us to propose the compre-
Figure 8. Sketch of graphite formation via a Ni-mediated catalytic reaction along a grain boundary in diamond. a–d represent different stages during the diamond-to-graphite transformation. Green arrows point to the release of C at the Ni-diamond interface, its diffusion along the Ni surface, and reconstruction as graphite planes. Red arrows indicate the movement direction of the Ni particle drilling a channel into the diamond. Compressive stresses (blue arrows) caused by volume expansion during Ni particle drilling act on the backside of the Ni particle, activate mechanisms of plasticity, and material push-out along the channel.

METHODS

Using focused microwave plasma enhanced chemical vapor deposition (MWPECVD equipped with an ellipsoidal cavity resonator Aixtron P6), nominally undoped NCD films were grown on p-type Si(100) wafer substrates with a 1.5 μm thick SiO₂ layer. Onto the NCD, 20 nm Ni films were deposited using a DC magnetron sputtering system. Next, the samples were annealed in a Carbolite tube furnace under low pressure of 10⁻⁶ mbar at the temperature of 1073 K for 10 min.

Raman spectroscopy was carried out at room temperature by using a Veeco alpha300 RA confocal microscope with 488 nm excitation wavelength. Raman spectra with a 60 s exposure time and 4 mW laser power were acquired. A pair of objective lenses, 100x/0.9 and 50x/0.55, and a 1200 g/mm grating were used in the measurements.

SEM investigations were performed using a Zeiss Supra SS VP operated at 10 kV employing the SE InLens detector and back-scattered BSE detector. In the case of the nonconductive as-grown diamond film the strong charging effects in the electron beam (limiting resolution, causing image distortions, and changing the overall contrast obtained by SE) were minimized by adjusting the focus and astigmatism slightly off the actual area of interest and keeping the exposure time as short as possible.

The specimens for (S)TEM-investigations were prepared in cross-sectional geometry by focused ion beam (FIB) sputtering using an FEI Quanta 3D FEG instrument. Before, protective 100 nm Au and 1 μm Pt layers were deposited onto the specimen surface to prevent beam damage during the preparation. Galium FIB settings during foil preparation were at 30 kV using successively lower ion probe currents ranging from 30 nA to 10 pA. The foil was thinned to a thickness of 40–50 nm and subsequently cleaned at FIB settings of 5 kV/40 pA and 2 kV/27 pA.

HRTEM and STEM was carried out at 200 kV using a JEOL JEM ARM200-F (S)TEM (equipped with Cs correctors for both the objective lens and the condenser system) and an FEI Titan 80–300 (S)TEM (Cs corrector for the objective lens). In BF STEM, the contrast strongly depends on the crystalline orientation of the different phases (diamond, Ni, graphite), while the HAADF STEM can be used to distinguish the different chemical species and densities of these phases. (S)TEM images were analyzed by using the Gatan DigitalMicrograph software. Fourier-filtered images were obtained by a Fast Fourier transformation (FFT), in which only the spatial frequencies of the diamond and graphite lattice were allowed to contribute to the filtered image.

Electrical transport measurement was performed in 4-probe configuration controlled by a source-meter Keithley 2635B supplying a constant current 100 nA. The temperature was changed from 300 to 4.2 K by moving a tubular sample chamber filled with He gas inside the 4He container. A Si diode was calibrated to measure the temperature, supplying a constant 10 μA current and measuring the voltage with a Keithley 2000 voltmeter.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b00692.

Author Contributions

All authors contributed to this work. V.S., S.T., T.W., B.R., A.K., O.R., and M.V. conceived and designed the study. M.V.

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and A.K. prepared the NCD films. S.T. and O.R. processed the samples. M.K. and V.V. deposited the protective Au films. S.T. carried out the SEM and Raman spectroscopy experiments. G.H. prepared the TEM foils by FIB. S.T., T.W., and M.C. carried out the TEM experiments. V.S. performed the electrical transport measurement and coordinated the research. S.T., T.W., and V.S. analyzed the data and wrote the manuscript and the Supporting Information. All authors discussed the results and commented on the manuscript.

**Notes**
The authors declare no competing financial interest.

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