Pick-up and drop transfer of diamond nanosheets

To cite this article: V Seshan et al 2015 Nanotechnology 26 125706

View the article online for updates and enhancements.

Related content

- Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping
  Andres Castellanos-Gomez, Michele Buscema, Rianda Molenaar et al.

- Pressure effects on the dissipative behavior of nanocrystalline diamond microelectromechanical resonators
  J T Santos, T Holz, A J S Fernandes et al.

- Dry transfer of chemical-vapor-deposition-grown graphene onto liquid-sensitive surfaces for tunnel junction applications
  Ying Feng and Ke Chen

Recent citations

- Growth and Isolation of Large Area Boron-Doped Nanocrystalline Diamond Sheets: A Route toward Diamond-on-Graphene Heterojunction
  R. Bogdanowicz et al

- Buckled diamond-like carbon nanomechanical resonators
  Matti Torni et al

- Transfer of an exfoliated monolayer graphene flake onto an optical fiber end face for erbium-doped fiber laser mode-locking
  Henrique Guimaraes Rosa et al
Pick-up and drop transfer of diamond nanosheets

V Seshan\textsuperscript{1,2,5}, J O Island\textsuperscript{1}, R van Leeuwen\textsuperscript{1}, W J Venstra\textsuperscript{1}, B H Schneider\textsuperscript{1}, S D Janssens\textsuperscript{3,4}, K Haenen\textsuperscript{3,4}, E J R Sudhölter\textsuperscript{2}, L C P M de Smet\textsuperscript{2}, H S J van der Zant\textsuperscript{1}, G A Steele\textsuperscript{1} and A Castellanos-Gomez\textsuperscript{1,6}

\textsuperscript{1} Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands
\textsuperscript{2} Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
\textsuperscript{3} Institute for Materials Research (IMO), Hasselt University, Wetenschapspark 1, B-3590 Diepenbeek, Belgium
\textsuperscript{4} IMOMEC, IMEC vzw, Wetenschapspark 1, B-3590 Diepenbeek, Belgium

Received 8 January 2015, revised 1 February 2015
Accepted for publication 2 February 2015
Published 5 March 2015

Abstract

Nanocrystalline diamond (NCD) is a promising material for electronic and mechanical micro- and nanodevices. Here we introduce a versatile pick-up and drop technique that makes it possible to investigate the electrical, optical and mechanical properties of as-grown NCD films. Using this technique, NCD nanosheets, as thin as 55 nm, can be picked-up from a growth substrate and positioned on another substrate. As a proof of concept, electronic devices and mechanical resonators are fabricated and their properties are characterized. In addition, the versatility of the method is further explored by transferring NCD nanosheets onto an optical fiber, which allows measuring its optical absorption. Finally, we show that NCD nanosheets can also be transferred onto two-dimensional crystals, such as MoS\textsubscript{2}, to fabricate heterostructures. Pick-up and drop transfer enables the fabrication of a variety of NCD-based devices without requiring lithography or wet processing.

Keywords: nanocrystalline diamond, nanosheets, electronic circuits, mechanical resonator, heterostructures, dry transfer

(Some figures may appear in colour only in the online journal)

1. Introduction

Diamond is a promising material that offers excellent mechanical, thermal and optical properties, such as a high Young’s modulus, a high thermal conductivity and broadband transparency \cite{1}. Pristine or undoped diamond is electrically insulating, however it can be turned into a semiconductor or superconductor by adding dopants such as boron, allowing diamond-based structures to be incorporated as functional components in electronic circuits \cite{2, 3}. In addition to being biologically compatible and inert to harsh environments, diamond can be functionalized chemically in various ways, as to enable bio-based electronic sensing \cite{4}. Moreover, diamond films, such as the nanocrystalline types, can be grown over large areas on non-diamond substrates, which significantly reduces the production costs \cite{5}. The attractive properties and robustness of diamond opens new avenues for interesting applications, which include high-quality nanophotonic circuits, ultra-sensitive force and mass transducers operating under extreme conditions, nanoelectromechanical contact switches and bio-nanomechanical devices \cite{6–10}. For many of these applications, diamond structures are typically fabricated using a top-down approach involving lithography, high-temperature annealing, etching and wet-chemical
processing [11]. Creating diamond-based devices with more sensitive materials such as two-dimensional (2D) atomic crystals is challenging because diamond growth requires high temperatures in a hydrogen rich atmosphere [12, 13]. Therefore, a technique that allows the integration of a diamond film into a pre-fabricated device is desirable and opens doors to more complex device architectures exploiting the properties of diamond films.

Here, we propose a versatile pick-up and drop method using visco-elastic stamps to transfer nanocrystalline diamond (NCD) nanosheets. The process is based on an all-dry technique that allows transfer of the NCD nanosheets, doped or undoped, from one substrate to another. The dry transfer technique has been used extensively to deposit 2D materials onto silicon-based substrates; here we use it to transfer NCD films onto a variety of substrates including metal electrodes, optical substrates; here we use it to transfer NCD nanosheets, typically 50 μm×50 μm in size, remain weakly adhered to the quartz surface.

2. Experimental section

2.1. Growth of NCD nanosheets

To grow the NCD nanosheets, we start with quartz substrates that are seeded with diamond nanoparticles [16]. The NCD films are deposited using a microwave plasma-enhanced chemical vapor deposition (CVD) process, using a conventional H2/CH4 plasma with methane concentration of ~4% (v/v). The microwave power is maintained at 3500 W, the substrate temperature at 510–560°C and the process pressure at 33–40 mbar. For obtaining the boron-doped NCD films used in electrical measurements, trimethylboron gas (boron to carbon concentration ratio of ~3000 ppm) is introduced in addition to H2/CH4 gases during the CVD growth process. The thickness of the NCD film is monitored in situ using a laser interferometer. It is important to note that the CVD process is stopped when the thickness of the NCD film on quartz substrate reaches ~180 nm. During the growth, a mismatch in the thermal expansion coefficient of the quartz substrate and the NCD film results in the accumulation of stress between the two materials. The conditions were purposefully chosen so that at a thickness of ~180 nm, this stress is sufficient to crack the film and to delaminate it from the quartz surface, forming numerous nanosheets. These nanosheets, typically 50 μm×50 μm in size, remain weakly adhered to the quartz surface.

2.2. Thinning of NCD nanosheets

The NCD nanosheets are thinned down using an oxygen (O2) reactive ion etching (RIE). A Leybold Heraeus system is used, with a dc bias voltage of approximately ~413 V. O2 gas flow of 30 ml min⁻¹ and pressure of ~20.7 mbar for ~10 min. This results in an etching rate of ~15 nm min⁻¹. The NCD nanosheets that are ~185 nm thick initially are reduced to ~55 nm. The whole transfer method including RIE is all-dry and no solvent is used throughout the manufacturing process in contrast with typical wet-etching techniques [11].

2.3. Thickness determination of NCD nanosheets

To determine the thickness of the NCD nanosheets before and after RIE processing, tapping-mode atomic force microscopy (AFM) is performed using a Digital Instruments D3100 AFM with a standard silicon cantilevers (spring constant of 40 N m⁻¹ and tip curvature of <10 nm).

2.4. Electrical transport measurements

The devices are electrically characterized using a two-terminal voltage bias in a Lakeshore Cryogenics probe station at room temperature and in ambient conditions.

2.5. Mechanical motion detection

The mechanical motion of the NCD nanosheet is measured using an optical interferometer, as described in more detail previously [15, 17]. The mechanical resonator is fabricated by transferring a NCD nanosheet onto a 100×100 μm² SiO2 square with a hole in its center, which has been lithographically defined and thermally evaporated on a silicon chip with a 285 nm SiO2 capping layer. While the back silicon surface acts as the fixed mirror (note that the silicon oxide is highly transparent), the nanosheet acts as the semi-transparent moving mirror, thus forming an interferometer. A Helium–Neon probing laser (λ = 632.8 nm) and a blue diode laser (λ = 405 nm) with an optical output below 1 mW for photothermal excitation of the resonators are focused on the suspended part of the nanosheet. On photothermal excitation, the motion of the NCD nanosheet changes the distance between the mirrors and via constructive or destructive interference modulates the reflected optical power. The intensity of the reflected optical signal is detected using a photodiode. All the measurements are carried out in vacuum (~10⁻⁵ mbar) to reduce viscous air damping.

3. Results and discussion

Figure 1(a) shows an optical image of a quartz surface with a collection of delaminated NCD nanosheets. A transparent visco-elastic stamp (GelFilm® by GelPak), similar to those used in nano-imprinting, is brought into contact with the sample supporting the NCD nanosheets using a micro-manipulator [14, 18]. Once in contact, due to the visco-elasticity, the stamp material can follow the topography of the
NCD nanosheets that are weakly adhered to the substrate. When the stamp is rapidly (in one quick motion) peeled-off, NCD nanosheets are transferred from the (substrate) surface onto the stamp. Figure 1(b) shows an optical image of the same sample after peeling-off the stamp displaying release of nanosheets from the substrate surface. The NCD nanosheets can be picked-up from the substrate by the visco-elastic stamp and transferred to another surface. Figures 1(c)–(f) show an example of a transfer process where a 185 nm thick NCD nanosheet has been deposited on the center of a lithographically defined structure (100 × 100 μm² SiO₂ square with a 15 μm diameter hole in the center, thermally evaporated onto a silicon chip with a 285 nm SiO₂ capping layer). The transfer process is carried out as follows using a method that was previously developed to transfer of 2D materials [14]. The stamp is mounted in a 3-axis micromanipulator with the surface containing the NCD nanosheets facing the substrate and aligned over the desired structure under a zoom lens (figure 1(d)). By lowering the manipulator, the stamp is first brought into contact with the substrate and then pressed slightly against the substrate. This step is followed by a slow peel-off process (approx imately 5–10 min) using the micro-manipulator, which transfers the NCD nanosheet over the user-defined position. Figures 1(e)–(h) show the transfer process of the nanosheet from the visco-elastic stamp to the pre-patterned SiO₂ substrate. Figure 1(h) shows the resulting NCD nanosheet transferred on the hole at the center of the SiO₂ square. The whole manufacturing process of peeling off and transfer of nanosheets is accomplished in 10–15 min. The transparency of the visco-elastic stamp along with the sub-micron control of the placement by using an optical microscope allows precise positioning of the NCD nanosheet over the holes. We have noticed that nanosheets with wrinkles or folds are prone to detach during the transfer step while flat and homogeneous nanosheets provide almost 100% transfer yields.

The pick-up and drop technique described above can be conveniently utilized to transfer/position NCD nanosheets with a sub-micron precision onto pre-patterned electrodes. We now turn our attention to the measurement of the

![Figure 1. Pick-up and drop transfer technique: optical microscopy images of the NCD nanosheets on a quartz substrate (a) before and (b) after stamping with a visco-elastic material. The arrows in panel (a) indicate the NCD nanosheets weakly adhered to the quartz substrate. (c)–(b) Series of optical microscopy images: (c) a pre-patterned SiO₂ substrate with a 100 nm thick oxide square with a hole (diameter: 15 μm) in the middle; (d) the selected NCD nanosheet aligned over the hole on a SiO₂ substrate using the micromanipulator; (e)–(g) the stamp brought in contact with the substrate and peeled-off using the micromanipulator; (h) the NCD nanosheet transferred over the hole on a SiO₂ substrate. The insets show a schematic of the stamping process [14].](image-url)
electrical properties of transferred boron doped (B-NCD) nanosheets. Although NCD is intrinsically insulating, its electronic properties can be tailored to a great extent by doping it with boron atoms [1]. For example, B-NCD becomes conducting and with high enough doping it displays superconductivity at $T_c = 2.1$ K [19]. This wide tunability of NCD (electronic) properties makes it very attractive for electronic applications and the possibility to transfer very thin doped-NCD films onto specific locations in a nanocircuit opens the door to the fabrication of complex device architectures. Furthermore, this technique could also offer a unique solution to repair micro-circuits by bridging the trenches or electrodes with B-NCD nanosheets. Figure 2(a) shows a scanning electron microscopy (SEM) image of a B-NCD nanosheet transferred between onto pre-patterned metallic electrodes (5 nm Ti/50 nm Au) on a Si/SiO$_2$ substrate. Two such devices with B-NCD nanosheets were fabricated and their electrical properties were characterized. Figure 2(c) shows the current versus voltage characteristic of the devices measured at room temperature displaying two terminal resistances of 3.9 k$\Omega$ and 6.6 k$\Omega$. The difference in the terminal resistances are attributed to the difference in the length and width of the electrodes. For the two fabricated devices, a resistivity of 6.0 $\Omega$. cm is obtained, which agrees reasonably well with the reported value of 3.4 $\Omega$. cm for a similar type of B-NCD films [20]. A zoom-in high angle SEM image of the nanosheet between the two electrodes is shown in figure 2(b). It is interesting to note that the nanosheet between the two electrodes is freely suspended. As many of the micro/nano electromechanical systems applications require structures to be free-standing and suspended from a substrate, our technique provides an all-dry (no solvent) and simple solution to fabricate suspended structures.

As a proof of concept to fabricate freely suspended NCD nanosheets, mechanical drumhead resonators are fabricated (figure 3). Five resonator devices with thicknesses of $\sim$55 nm and $\sim$185 nm and diameters from 6 $\mu$m to 15 $\mu$m were measured. The resonant motion of the NCD resonators are detected using an optical interferometer [15, 17]. Figure 3(a) shows the measured mechanical magnitude (circles) and phase (squares) spectra, with the corresponding optical microscopy image for the devices with the thickness of $\sim$55 nm and (hole) diameters of 15 $\mu$m. The resonance frequencies and Q-factors are extracted by fitting the measured data to a damped-harmonic oscillator model, indicated by solid lines in figure 3(a). The resonance frequency of the devices is found to be in the range of 5–20 MHz (depending on thickness and diameter) with Q-factors between 40 and 155 (figures 3(a)–(d)). For devices with identical thickness measured under the same experimental conditions, we observe a significant increase of the Q-factor with the resonator diameter. This suggests that the Q-factor is limited by clamping losses.

To characterize the obtained NCD resonators further, the resonance frequency ($f_0$) is measured as a function of the resonator thickness ($t$) and diameter ($d$). Figure 4(a) shows the measured resonance frequency versus the (resonator) thickness over the square of hole diameter for $\sim$55 nm and $\sim$185 nm thick NCD mechanical resonators. The uncertainty shown in the error bar in figure 4(a) is due to the roughness of the NCD flake, which is approx imately $\pm$15 nm (figure 4(b)).

For a plate-like circular resonator clamped around its perimeter, the frequency is given by [21]:

$$f_0 = \frac{10.21}{\pi} \sqrt{\frac{E}{3\rho(1-\nu^2)}} \frac{t}{d^2},$$

where, $E$ is the Young’s modulus, $\rho$ is the mass density and $\nu$ is the Poisson’s ratio. For typical values for polycrystalline diamond of $E$ ($\approx$304 GPa) [22], $\rho$ (3500 kg m$^{-3}$) [22] and $\nu$ (0.12) [23], the resonance frequencies calculated from equation (1) are shown by the solid line in figure 4(a). The good correspondence between the measured data and this solid line indicates that the resonators indeed behave as circular plates whose dynamics is thus dominated by bending rigidity and not by their initial pre-tension. This is a desirable feature for nanomechanical resonators as the bending rigidity can be easily controlled by geometrical factors while the initial pre-tension typically varies from device to device. For a pre-tension dominated device, the second-order eigenmode is expected to be at 1.59 $f_0$ whereas for a bending rigidity dominated device, this value is expected to be around 2.08 $f_0$ [15, 21]. Therefore, to further confirm the plate-like behavior of the NCD resonators, we measured the resonance frequencies of higher-order eigenmodes. Here we observe, for the second mode, resonance frequencies at 1.91–2.06 $f_0$,
which is in good agreement with the expected value for a circular plate (figure 5).

To further illustrate the versatility of our pick-up and drop transfer technique, a single NCD nanosheet ($\approx 185$ nm) is transferred onto the core of a multimode optical fiber. Figure 6 shows an optical image of the fiber (a) prior to and
(b) after stamping the NCD nanosheet and (c) their corresponding optical transmission spectra. The transmittance \( T = \frac{I}{I_0} \), calculated from the transmission spectra, at 750 nm is \( \approx 60\% \) which is comparable to reported values in literature for NCD films of similar thickness \( (\approx 62\%) \) [24]. This example demonstrates that this rather simple technique can be used to study the optical properties of NCD films and even to integrate these films as optically active components of an optical setup. The stamping technique can also be used to manufacture heterostructures through artificially stacking NCD nanosheets onto 2D materials such as MoS\(_2\). Figures 6(d)–(e) display optical images of the MoS\(_2\) flake on a Si/SiO\(_2\) substrate followed by stacking of the NCD nanosheet on top of MoS\(_2\) flake. The stamping method promises new applications and device components, such as electrodes, active materials, barrier materials and dielectric materials derived from stacking a wide variety of 2D materials in combination with NCD [25, 26].

Additionally, we show that this relatively simple transfer technique can be employed to place NCD nanosheets directly onto pre-fabricated electrodes. As the NCD nanosheets can be transferred in the final step, it allows one to integrate NCD nanosheets in complex device architectures or in devices requiring very harsh fabrication processes or chemical treatments. Interestingly, the transferred NCD nanosheets can be freely-suspended without collapsing, making it possible to use this technique to fabricate NCD resonators. We characterize these resonators and measure frequencies of 5–20 MHz (depending on thickness and diameter) and Q-factors between 40 and 155. Finally, we demonstrate the flexibility of the pick-up and drop technique by transferring a NCD nanosheet onto the core of an optical fiber and on top of a few-layer MoS\(_2\) flake, illustrating how this technique can be employed to transfer NCD nanosheets onto non-conventional substrates widening the range of applications of thin NCD films.

4. Conclusion

In summary, we demonstrate a versatile transfer technique based on an all-dry visco-elastic stamping to pick-up NCD films (as thin as 55 nm) from one substrate and to deposit them onto a specific location on another substrate.

Acknowledgments

V Seshan and J O Island contributed equally to this work. The authors thank Shun Yanai (Delft University of Technology) for his help with the SEM and Milos Nesládek (Hasselt University) for insightful discussions. The authors would like...
to acknowledge the funding agencies: the Delft University of Technology, the Dutch organization for Fundamental Research on Matter (FOM), the Research Program G.0456.12N of the Research Foundation-Flanders (FWO), the FP7-Marie Curie Project PIEF-GA-2011-300802 (‘STRENGTHNANO’), NanoNextNL (a micro and nanotechnology consortium of the Government of the Netherlands and 130 partners) and the European Union’s Seventh Framework Programme (FP7/2007-2013) under Grant Agreement n° 318287, project LANDAUER.

References