

## CORRELATED MICROSCOPY OF ELECTRONIC AND MATERIAL PROPERTIES OF GRAPHENE GROWN ON DIAMOND THIN FILMS

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### Abstract

We study formation and properties of graphene grown on diamond films with a prospect for large area deposition and devices of graphene. Nanocrystalline diamond thin films (grain size ~ 200 nm) are coated with a thin Ni layer (nominal thickness ~ 20 nm) and heated to 900°C in a forming gas atmosphere (H<sub>2</sub>/Ar) to initiate a thermally driven catalytic transformation of the diamond surface into graphene by a reaction of Ni with carbon. The samples are cleaned from residual Ni after the catalytic transformation. We employ scanning electron microscopy, Raman micro-spectroscopy, and Kelvin probe force microscopy showing how diamond and grain boundaries influence the graphene growth as well as graphene material, structural, and electronic properties.

**Keywords:** Graphene, diamond, microscopy, micro-spectroscopy, electronic properties

### 1. INTRODUCTION

Two allotropes of carbon, the sp<sup>2</sup>-bonded two-dimensional graphene and sp<sup>3</sup>-bonded three-dimensional diamond have both attracted a significant technological and scientific attention. For graphene, the electronic properties such as high carrier mobility, saturation velocity, mechanical strength and chemical stability have driven the enormous interest, whereas for diamond, the extraordinary combination of intrinsic properties (hardness, chemical stability, wide range optical transparency, semiconducting properties, etc.) has been in the spotlight. Due to outstanding properties, both materials are considered promising in the fields of nano-electronics, bio-electronics, spintronics, photonics, and life sciences. Yet industrial scale applications taking advantage of the above specific and unique features are still lacking. To realize possibly large impact of these materials in the respective applications, there is a high demand for developing technological procedures resulting in their fabrication with well-defined bulk and/or surface properties. Moreover, combining both materials in one system, as represented for instance by graphene-on-diamond composite, can provide new perspectives where novel devices will benefit from complementary properties of graphene and diamond.

Since graphene has a zero bandgap, devices fabricated from it have a small on-off ratio. The development of a reliable technique to create a sizable gap without degrading the electronic properties of the material remains challenging so far. Moreover, electronic properties can be affected by nearby materials. In that respect, graphene-on-diamond structures have attracted much attention recently [1]. Compared with SiO<sub>2</sub> and other substrates, diamond has low charged surface states, few impurities, and high phonon energy. Graphene on monocrystalline diamond (111) surface behaved as a semiconductor with both finite gap and linear band dispersion and exhibited both p-type and n-type doping [2]. Electronic devices composed of hybrid graphene-diamond structures, which were fabricated by transferring graphene on top of diamond layers, demonstrated very promising performance [3]. Thus diamond appears as a suitable substrate material for graphene. Under particular conditions graphene can be formed by thermal processes on diamond directly, thereby avoiding

wrinkling and contamination during the substrate transfer process [1], [4]. Compared with SiO<sub>2</sub>, SiC, and most other substrates, diamond has low charged surface states, few impurities, and high phonon energy (165 meV). Since the monocrystalline diamond substrates are still too expensive and too small (typically few mm in size) for industrial applications, the focus is directed to layers of nanocrystalline diamond.

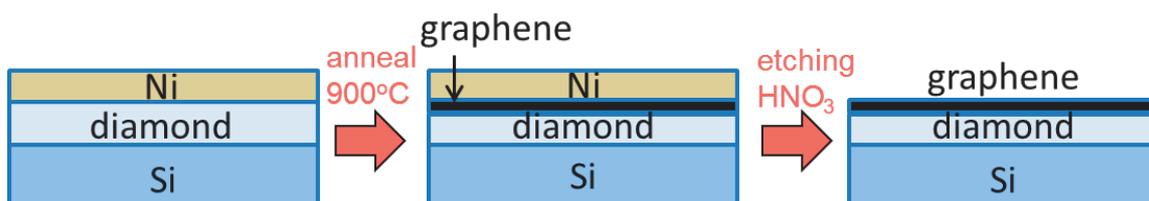
Recent report showed that graphene can be formed on an ultrananocrystalline (the grain size of 2-5 nm) diamond thin film by thermally driven catalytic process in wafer size [1]. The process does not involve a graphene transfer from another substrate while intrinsic diamond can provide also electrical insulation. The current-carrying capacity of graphene on ultrananocrystalline diamond was as high as 18 μA/nm<sup>2</sup> even under ambient conditions. The results indicated that graphene's current-induced breakdown is thermally activated. Replacing conventional SiO<sub>2</sub> substrate with diamond also substantially improved radio frequency characteristics of graphene transistors, leading to a new planar sp<sup>2</sup>-on-sp<sup>3</sup> carbon-on-carbon technology. Nevertheless, structure and interactions at the interface of graphene and diamond still remain unclear and reliable growth across large areas represents a challenge.

In this work we demonstrate a formation of graphene on nanocrystalline diamond (NCD) thin films by Ni induced catalytic process and compare it with similar process on monocrystalline diamond. We characterize these carbon-based layered composites by a number of microscopic techniques and Raman micro-spectroscopy. We focus in particular on a correlation of structure, composition and electronic properties on microscopic level by merging data from the diverse methods.

## 2. MATERIALS AND METHODS

The NCD thin films with mean grain size of 200 nanometers were prepared by chemical vapor deposition in microwave plasma (Aixtron P6 reactor) on p-type Si wafer substrates [5]. The diamond chemical vapor deposition (CVD) process was performed in two steps: The first interfacial layer was grown using 1% of CH<sub>4</sub> in 300 sccm of H<sub>2</sub>, 30 mbar, power 2500 W, temperature 300 °C, duration 15 min. The second layer was grown using 5% of CH<sub>4</sub> in 300 sccm of H<sub>2</sub>, 100 mbar, power 4500 W, temperature 950 °C, duration 60 min.

The as-deposited diamond films were coated with a thin Ni layer (nominal thickness ~ 20 nm) and heated to 900°C for 10 min in a forming gas atmosphere (H<sub>2</sub>/Ar) to initiate a catalytic transformation process. **Figure 1** shows an idealized schematic drawing of the Ni-coated diamond films before and after the annealing process. After the graphene growth process the samples were cleaned from residual Ni catalyst by using wet chemical etching in 10% HNO<sub>3</sub>.

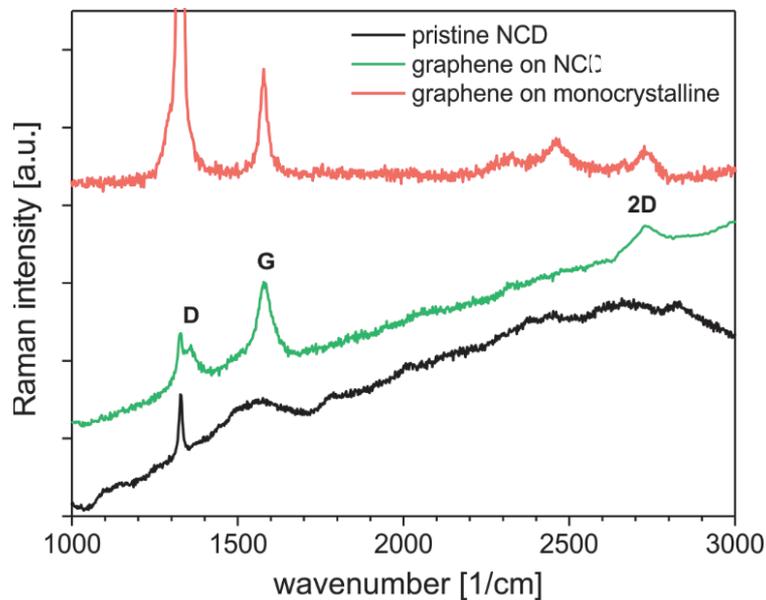


**Figure 1** Schematic drawing of diamond surface transformation to graphene

To characterize structural, and electronic properties of graphene on diamond we employed scanning electron microscopy (SEM) of secondary electron emission, Raman micro-spectroscopy (excitation wavelength 473 nm), and atomic and Kelvin probe force microscopy (AFM/KPFM, using Cr/Pt coated silicon tips BSMulti75E-G). This methodology was previously successfully established for characterizing CVD graphene deposited on polycrystalline Cu foil, showing variations in graphene quality and doping in dependence on the Cu grain surface structure and composition [6].

### 3. RESULTS AND DISCUSSION

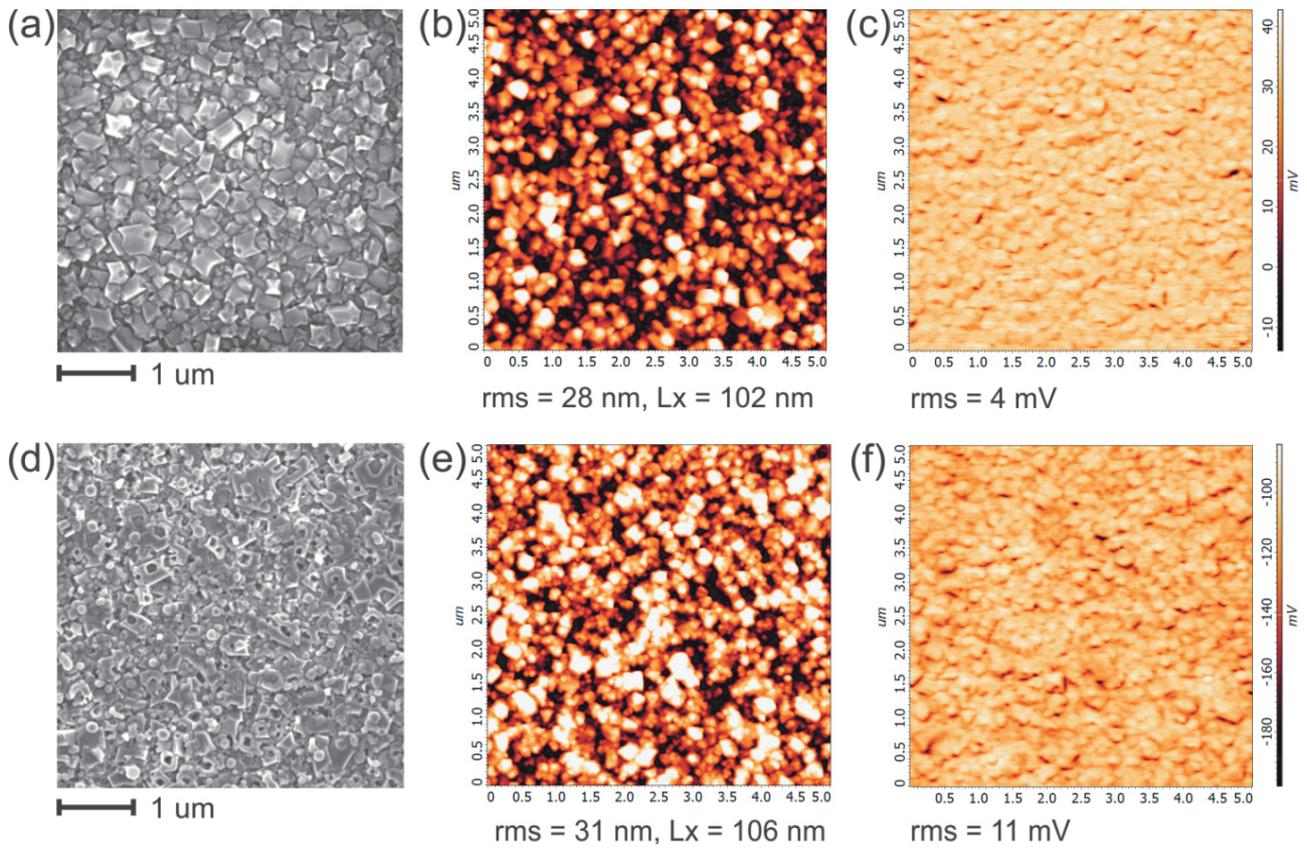
**Figure 2** shows Raman spectra from the NCD thin film before and after the catalytic transformation process. Spectrum from monocrystalline diamond after similar process is shown for comparison as well. The diamond character of the pristine NCD layer is confirmed by a single narrow peak at  $1330\text{ cm}^{-1}$  in the Raman spectrum. After the transformation process the sharp peak of diamond is superposed on a wider peak resulting from defects in a graphitic structure - the dispersive D mode at around  $1350\text{ cm}^{-1}$ . In addition, two other graphitic features are resolved in the spectrum: the G and 2D peaks. The two peaks evidence formation of graphene on diamond. The ratio of G/2D intensities is larger than 1, which indicates few layer graphene. It is noticeable that nanocrystalline diamond provides the most pronounced 2D graphene peak as well as lower G/2D intensity ratio compared to monocrystalline diamond. Most likely, a large amount of grain boundaries acts as a carbon source for the graphene growth [1].



**Figure 2** Characteristic Raman spectra on nanocrystalline diamond substrate before and after the graphene formation process and wet etching of Ni catalyst. Spectrum for the graphene prepared on monocrystalline diamond substrate is shown for comparison as well

Microscopic study of morphology, material quality, and electronic properties of graphene on the NCD film is presented in **Figure 3**. **Figure 3a** shows SEM image of the NCD surface morphology prior to the Ni deposition. Despite the small grain size of  $\sim 200\text{ nm}$ , the grains exhibit well developed crystal facets. **Figure 3d** shows SEM image of the surface morphology of the NCD film after the catalytic transformation and removal of residual Ni. The originally smooth facets of the diamond nanocrystals now exhibit grooves with a size of several tens of nm. This indicates an inhomogeneous etching due to the thermal reaction of Ni with carbon.

**Figure 3** also shows corresponding AFM surface morphology and KPFM map of surface potential across  $5 \times 5\ \mu\text{m}^2$  area on the NCD film before and after the transformation process. The difference in AFM images is well correlated with the features in SEM images. More rounded features after the graphene growth are thus related to dissolution of diamond by nickel rather than by graphene which is able to follow the surface morphology closely [6]. The values below the images show root mean square (rms) of surface roughness and KPFM potential. Lateral feature size is characterized by the  $L_x$  value of autocorrelation function. The values do not change significantly for the morphology. On the other hand, the rms value of surface potential increases almost 3 times.

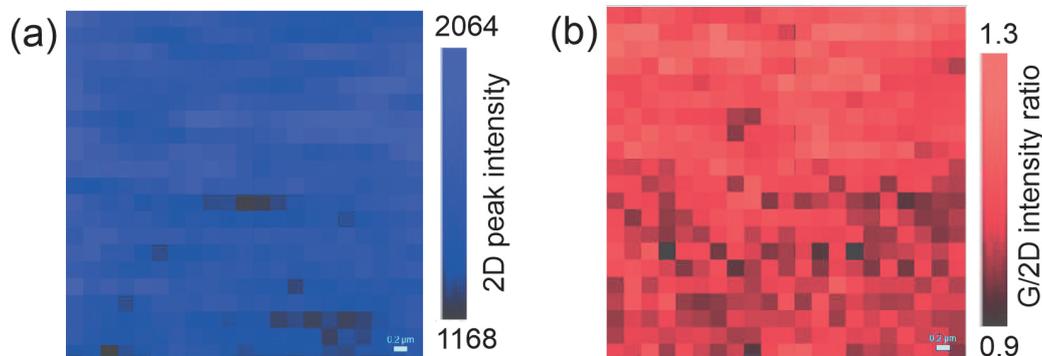


**Figure 3** Characteristic SEM and AFM surface morphology and corresponding KPFM map of surface potential on nanocrystalline diamond thin film (a, b, c) prior to and (d, e, f) after the graphene growth process on  $5 \times 5 \mu\text{m}^2$  area. The values below the images show root mean square of surface roughness and KPFM potential. Lateral feature size is characterized by Lx value of autocorrelation function

This effect can be elucidate by looking at the micro-Raman maps of 2D peak intensity and G/2D peak intensity ratio across the similar  $5 \times 5 \mu\text{m}^2$  area, which are shown in **Figure 4**. The maps contain some fluctuations yet they are generally uniform, not exhibiting correlation with surface morphology. In numbers the G/2D ratio (the best parameter for assessing graphene thickness) varies between 0.9-1.3. This means that graphene is composed of more than 3 layers and the thickness is relatively uniform. On the other hand, the KPFM is correlated with the surface morphology. The 3x increased rms of the surface potential measured on graphene thus most likely corresponds to local differences in graphene doping, charge carrier density, and/or structural defects. A sizable disorder in carrier density is observed even in the best single layer graphene samples either suspended [7] or placed on hexagonal boron nitride substrates [8]. In the case of NCD substrates, the differences can be caused by underlying NCD film morphology (roughness, facets, grain boundaries). Thus we can expect variations due to mechanical strain or grain boundaries in graphene [6].

Overall level of doping in graphene was evaluated by comparing the mean potential values. On the NCD film it was +32 mV initially and -110 mV after the graphene formation. KPFM measurements on reference Au substrate before and after the measurements on NCD and graphene samples exhibited variation of the mean potential within 10 mV. By using Au work function, the KPFM potentials can be thus reliably recalculated to work functions. The work function increased from initial 4.9 eV on NCD (a typical value) to 5.1 eV after the graphene growth process. The relatively high work function of graphene on NCD compared to suspended graphene (4.6 eV) indicates its significant p-doping. The value of 5.1 may make such graphene-on-diamond structures suitable for instance as replacement for transparent conducting oxide electrodes [9]. Such increased work function was achieved previously by intercalation of Ni grown graphene which resulted into high surface

potential inhomogeneity though (order of 100 mV) [9]. Thus diamond seems to provide better work function homogeneity (within 11 mV rms) and may avoid the intercalation process.



**Figure 4** Micro-Raman maps of (a) 2D peak intensity and (b) G/2D peak intensity ratio across the 5x5  $\mu\text{m}^2$  area with the scanning step of 200 nm along X and Y axes

#### 4. CONCLUSION

We presented a successful graphene growth on nanocrystalline diamond films via transformation in a solid state reaction using Ni film as the catalyst. Raman spectra showed that the transformed surface is covered by about 3 graphitic layers for the employed process conditions. The G/2D ratio was better than for the reference monocrystalline diamond substrate. The graphene on nanocrystalline diamond was p-doped with a high work function of 5.1 eV, which was highly uniform (11 mV rms). The potential fluctuations can be attributed to several factors such as differences in local doping, charge carrier density or structural defects (such as grain boundaries) due to underlying nanocrystalline diamond substrate. Even though not all aspects of the growth mechanism as well as material properties are yet fully understood, our work shows that graphene on thin film diamond can be developed into promising platform for various novel devices.

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