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# CHARGED MICRO-PATTERNS ON NANOCRYSTALLINE DIAMOND ARE WELL DEFINED BY ELECTRICAL CURRENT APPLICATION

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We apply atomic force microscope for local electrostatic charging of oxygen-terminated nanocrystalline diamond (NCD) thin films deposited on silicon by regulated electrical current application. The NCD films have sub-100 nm thickness and 60% relative  $sp^2$  phase content. The charge is injected by constant current application. Induced electrical potential contrast is then evaluated by Kelvin Force Microscopy (KFM) which shows well-defined homogeneous features and a sub-linear increase of surface potential with increase in electrical current. We suggest limitation by field-induced detrapping.

## 1. Introduction

As regards local and intentional electrostatic charging, diamond has been only little investigated [Čermák *et al.*, 2008, Verveniotis *et al.*, 2009, 2010, 2011] even though it exhibits a unique set of properties for applications such as radiation detectors, UV detectors, or field-effect transistors. Both positive and negative persistent potential changes were observed on nanocrystalline diamond (NCD) by Kelvin force microscopy (KFM) [Čermák *et al.*, 2008], unlike in silicon thin films [Rezek *et al.*, 2003]. This has been attributed to the capacitor-like behavior of the NCD films [Čermák *et al.*, 2008]. Comparing charging of NCD films prepared on gold [Čermák *et al.*, 2008] and silicon [Verveniotis *et al.*, 2009] substrates demonstrates that the charging

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is not due to the substrate itself as could be argued in the case of silicon substrates. The charging has been also shown to be more effective when the NCD films contain more  $sp^2$  phase [Verveniotis *et al.*, 2010]. Yet maximal induced electrostatic potential contrast has been reported to vary depending on a position on the sample [Verveniotis *et al.*, 2011]. In addition, charged patterns were not homogeneous showing a variation up to 50 % of the maximum potential. This may depend on the local material properties, charge stability as well as to the tip-surface junction quality. As the threshold for electrostatically-driven assembly of nanoparticles on charged patterns is 1 V for both polarities, the maximum potential contrast variation represents a bottleneck towards reliable applications [Verveniotis *et al.*, 2011].

Previous work employed constant voltage application for local diamond charging [Čermák *et al.*, 2008, Verveniotis *et al.*, 2009, 2010, 2011, 2012]. However, as conductivity of the NCD samples varies even in the nanoscale due to presence of grains ( $sp^3$  bonded carbon-diamond), grain boundaries ( $sp^2$  bonded carbon-graphite) [Verveniotis *et al.*, 2010] and complex sub-surface morphology [Verveniotis *et al.*, 2011], this approach did not introduce the same amount of charges all over the working area. In order to ensure similar exposure conditions and overcome the tip-surface junction-related problems it may be beneficial to charge NCD by using constant current instead of voltage. Implementing such technique in microscale, specifically in Atomic Force Microscopy (AFM), is challenging

In this work we show that this approach is indeed feasible and that the charging can be controlled by the applied electrical current. We demonstrate that it can help to overcome the reproducibility issues since constant current exposes the working area to similar number of charge carriers irrespective of local morphology, material properties and tip-surface junction quality. Results after charging are analyzed by evaluation of surface potential and electrical current maps.

## 2. Materials and Methods

The substrates used in this work for NCD growth were  $5 \times 10 \text{ mm}^2$  conductive p-doped silicon wafers nucleated by water-dispersed detonation diamond powder of 5 nm nominal particle size (NanoAmando, New Metals and Chemicals Corp. Ltd., Kyobashi) using an ultrasonic treatment for 40 min. NCD films were prepared by microwave plasma chemical vapor deposition using the following parameters: substrate temperature  $820^\circ\text{C}$ , deposition time 16 minutes, microwave plasma power 900 W,  $\text{CH}_4:\text{H}_2$  dilution 3:300. Resulting thickness was 70 nm as measured by ellipsometry. After the deposition, the diamond films were oxidized in r.f. oxygen plasma (300 W, 3 min) [Rezek *et al.*, 2009]. Raman spectroscopy showed 60% relative  $sp^2$  phase content in the films [Verveniotis *et al.*, 2011].

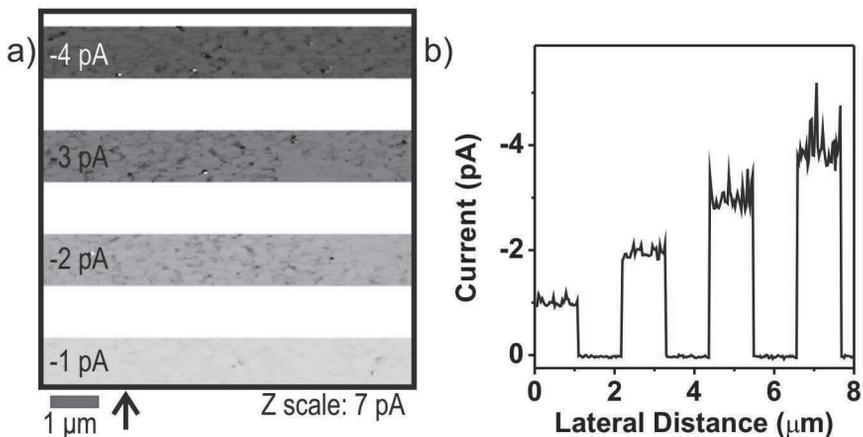


FIGURE 1. (a) Current map in a regulated current charging experiment ( $I_s$  values are indicated within the stripes). (b) Cross section profile of the current as indicated by the arrow in the current map.

Charged micro-patterns were prepared by an AFM (N-TEGRA system by NT-MDT) scanning in contact mode. We used a special AFM regime that enabled constant current application in the range of  $-1$  to  $-4$  pA. The constant current is maintained by a secondary feedback circuit which was adjusting the applied voltage. Conductive, diamond coated silicon probes were used (DCP11 by NT-MDT). Applied contact forces were  $\approx 100$  nN. The scan speed was always  $5 \mu\text{m/s}$ . Kelvin Force microscopy (KFM) was then used to detect electric potential differences across the sample [Rezek *et al.*, 2005]. Relative humidity and temperature during all AFM experiments were in the ranges of 20–32% and 22–26 °C.

### 3. Results

Figure 1a shows the current map during the charging experiment, while implementing the secondary feedback for current regulation. For this experiment we used four different current set-point ( $I_s$ ) values:  $-1$ ,  $-2$ ,  $-3$ , and  $-4$  pA from the bottom to the top. The voltage that gave rise to the constant current was in the range of  $-14$  to  $-16$  V.

The adjacent non-zero  $I_s$  states are separated by areas of the same size where  $I_s$  was zero (white stripes in the image). We can see that the current fluctuates above and below the set-point (darker and brighter spots in each stripe). Magnitude of this fluctuation is increasing at higher set-points. The fluctuations are clearly demonstrated in Figure 1b where we see the cross section of current indicated by the arrow in Figure 1a.

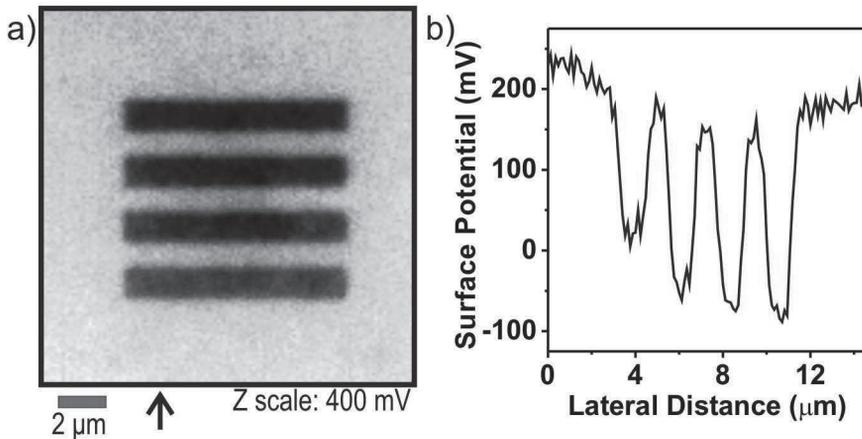


FIGURE 2. (a) Surface potential map as a result of the charging experiment illustrated in Figure 1. (b) Cross section of surface potential as indicated by the arrow in the potential map.

The result of this charging experiment can be seen in the KFM map and cross section in Figure 2 which were measured immediately after charging. Even though a slight fluctuation is evident within each “stripe” (up to 80 mV vs. 60 mV of the uncharged background), the charged features are relatively homogeneous compared to previous results [Verveniotis *et al.*, 2011]. Note that such charged patterns on NCD are persistent over time despite the charge decay that occurs due to sample exposure to the ambient atmosphere [Čermák *et al.*, 2008, Verveniotis *et al.*, 2009].

Quantitative evaluation of the KFM measurement is shown in Figure 3. The blue curve (triangles) shows average potential contrast values deduced from each individual stripe, as a function of the constant charging current,  $I_s$ . The induced potential contrast increases with  $I_s$  but the magnitude of that  $\Delta V$  is smaller for higher set-point values. For example,  $-2$  pA produced  $-55$  mV higher negative potential compared to  $-1$  pA. Higher set-points gave an increase of  $-25$  mV ( $-2$  pA to  $-3$  pA) and  $-10$  mV ( $-3$  pA to  $-4$  pA) as seen from the red curve (circles).

#### 4. Discussion

The results show that charging of NCD with control of the electrical current is possible despite various technical challenges. In order to establish a constant current, the bias voltage has to be constantly monitored and adjusted with respect to the local material properties. Given the complicated nature of the film (conductive grain boundaries, insulative grains) and thus rapidly changing RC constant of the system being measured, the feedback must be very fast and accurate in order to stabilize

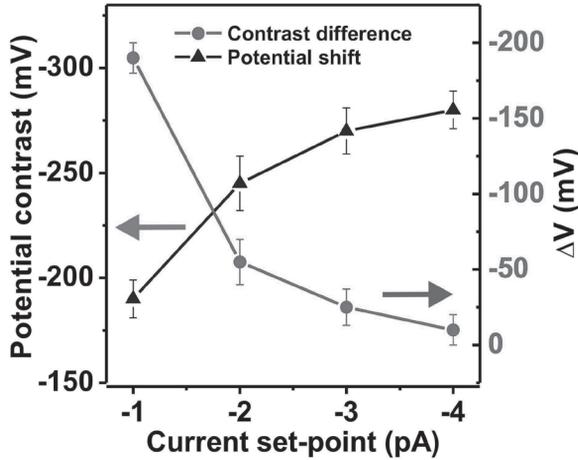


FIGURE 3. Average surface potential measured from each stripe of Figure 2a and differences between the induced potential contrast at successive current set-point values.

the current. Moreover the AFM tip stays over one spot for only 6 msec (scan speed  $5 \mu\text{m/s}$ , scan size  $8 \times 8 \mu\text{m}$ , scanlines 256, points per scanline 256) which introduces yet another challenge to the feedback response. Note that the employed scan speed is a compromise between current stability (needs slow scans) and measurement time.

We can see in Figure 1 that the charging is more homogeneous compared to past results [Verveniotis *et al.*, 2011, 2012]. This is attributed to the constant current application which improved the results of the process qualitatively.

The increased current fluctuation at higher  $I_s$  can be explained by the increased bias which produces bigger differences between the current that flows through the grain boundaries and through the grains. Since for such NCD films (grain size  $< 100 \text{ nm}$ ) the AFM tip will encounter numerous transitions between grains and grain boundaries within few tens of msec, the inherently imperfect feedback controlling the current cannot respond that fast.

The findings of Figure 2 reveal a trend between the charging current and the induced potential contrast. Nevertheless, the potential difference does not increase linearly with the current. Its increment is constantly reduced for higher current values. As the amount of injected charge does increase linearly ( $-1 \text{ pA}$  more current in sequential stripes,  $I = Q/t$  with exposure time being constant) the KFM map and average potential plot (Figure 3) indicate that we are approaching the saturation point. Similarly, previous work conducted on the same sample indicated that saturation occurs during constant voltage charging [Verveniotis *et al.*, 2009]. However, the saturation appears at around  $-25 \text{ V}$  for this polarity. Moreover, storage of much higher amounts of charge, accounting for potential shifts up to  $1.2 \text{ V}$ , has been systematically demonstrated on this thin film [Verveniotis *et al.*, 2010, 2011]. One possible explanation is

that the observed saturation effect might be due to field-induced detrapping which becomes more evident when increasing the effective electric field [Rogalla *et al.*, 1997]. Indeed, in another experiment, when we applied a constant current of  $-50$  pA (adjusted voltage was  $-37$  V), the potential contrast was only  $-175$  mV ( $\pm 13$  mV), i.e. less than what was observed here for  $-1$  pA.

## 5. Conclusion

Local electrostatic charging of NCD by constant current application was performed by implementing a secondary feedback controlling the bias voltage while scanning in AFM. Results of this methodology are more homogeneous charged patterns, as the charge fluctuations are now significantly smaller than what was observed before in constant voltage patterns [Verveniotis *et al.*, 2011] and they are comparable with fluctuation of the uncharged background. We assume that the application of constant current minimized the effects of tip-surface contact quality fluctuations.

Induced potential contrast increases with applied current but the trend is sub-linear despite the linear increase of the charge carriers injected to the system. This is probably due to field-enhanced detrapping which becomes more pronounced at higher applied current (thus voltage). This seems to limit the maximum charge contrast. We plan to investigate this effect by repeated or slower charging, to inject more charge per unit area while the electric field is kept small.

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