Electron induced modification of the surface electrochemical properties of diamond electrodes

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A novel method has been developed to modify the surface properties of boron-doped CVD diamond electrodes by electron stimulated desorption (ESD) of hydrogen and oxygen from as grown diamond surfaces allowing the selective electrochemical silver deposition on the areas not irradiated with electrons.

Boron-doped CVD diamond is a very promising material in areas such as electrochemistry and electronics owing to very useful properties, such as extreme hardness, chemical inertness, very high electrical and heat conductivity and negative electron affinity (NEA) when hydrogen terminated. In this study, results are presented on the effect of the electron stimulated desorption of hydrogen and oxygen from boron-doped diamond surfaces on the electrochemical characteristics, monitored by the silver deposition on areas irradiated and not irradiated with high energy electrons in a scanning electron microscope (SEM). A correlation between changes in electron affinity and electrochemical activity is observed.

Highly conductive boron-doped diamond films were deposited on 5 mm diameter tungsten substrates from a gaseous feed of diborane and 1% methane in hydrogen using a hot filament assisted CVD reactor as described previously.[1] The boron-doped diamond surface was irradiated by an electron beam of an energy ranging from 1 to 25 keV and a current density ranging from *ca.* 93 mA cm^{-2} to 60 A cm^{-2} at a background pressure of *ca.* 10^{-6} mbar at room temperature. SEM images of treated and untreated areas after electrochemical deposition of silver on the surface of the boron-doped diamond are presented in Fig. 1. An interesting feature shown in the SEM images is the well defined dark irradiated area in contrast to the much brighter surroundings. In a XPS study, Cui *et al.*[2] reported electron beam stimulated desorption of hydrogen from single crystal diamond (111) surfaces. They showed that H-terminated diamond has a negative electron affinity (NEA) of $\chi = -1.27$ eV and that electron irradiation desorbed the terminal hydrogen as a function of time giving the diamond surface a positive electron affinity of $\chi = +0.4$ eV (less brightness in SEM images) without graphitising the surface. NEA materials such as hydrogenated diamond when irradiated with energetic electrons, exhibit very high secondary electron emission.[3] Hence, the darker feature shown on the SEM image can be attributed to lower secondary electron emission and is therefore indicative of a hydrogen depleted diamond surface. Interestingly, in the backscatter mode no shading is observed. The backscatter electrons have much higher energy than secondary electrons and so are insensitive to the energy barrier which exists at the surface. This is consistent with a surface modification involving a change in χ.

Based on the work by Cui *et al.*[2] it is proposed that the electron beam irradiation desorbs hydrogen from a well defined area with a resolution approximating that of the electron beam (*ca.* 0.5 nm) from the hydrogen terminated diamond surface. Energy dispersive X-ray spectrometry (EDX) was performed in order to estimate the oxygen concentration of the irradiated area compared to the surrounding surface. Although EDX is not highly surface sensitive, a comparison clearly indicates that the electron irradiated area, after the silver deposition process, exhibits a very low O/C ratio (O below the signal to noise level) and therefore had practically no oxygen functionalities on the surface. The O/C peak area ratio in the EDX spectrum for the area not irradiated was significantly higher with a value of *ca.* 5%. It can be concluded that the electron beam actively removes hydrogen, oxygen, and probably other impurities from the surface.

In order to study the effect of the electron beam on the electrochemical characteristics of the surface of the boron-doped diamond, silver was deposited electrochemically. Fig. 2 shows cyclic voltammograms for three consecutive potential cycles with a scan rate of 0.1 V s^{-1} for the reduction/oxidation

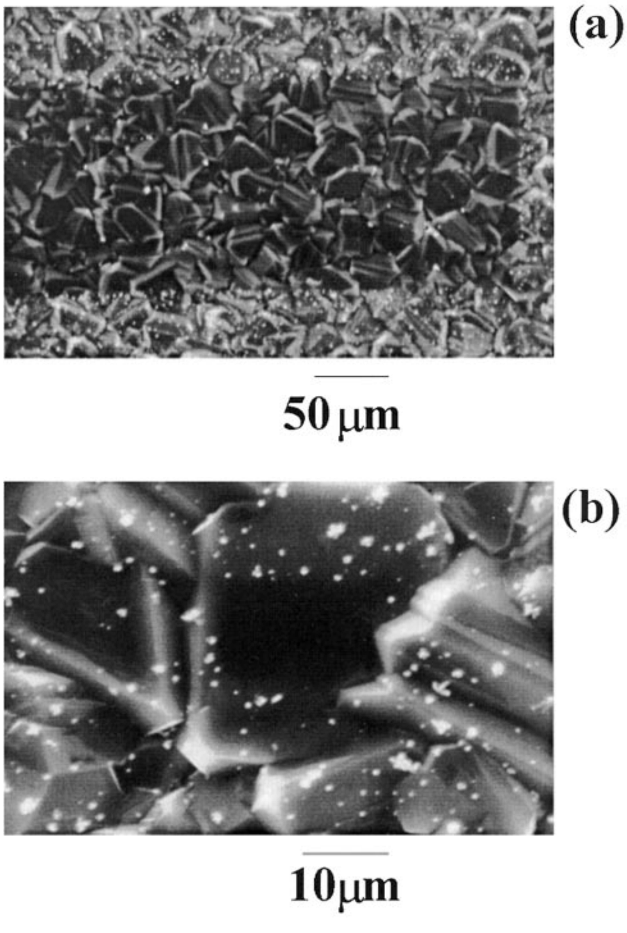

Fig. 1 SEM images of boron-doped diamond electrode surfaces after electrochemical deposition of silver from 1mM $AgNO_3$ in aqueous 0.1 M HNO_3 at a potential of $E = +0.17$ V *vs.* SCE (deposition time 3 min, irradiated with electrons of (a) an energy of 1 keV and a current density of *ca.* 93 mA cm^{-2} for 30 min and (b) an energy of 25 keV and a current density of *ca.* 60 A cm^{-2} for 5 min).

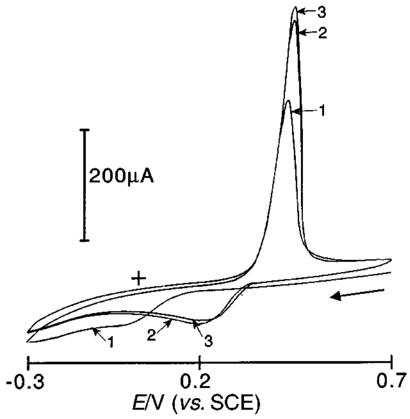

Fig. 2 Three consecutive cyclic voltammograms recorded with a scan rate of 0.1 V s^{-1} for the reduction/oxidation of 1mM $AgNO_3$ in aqueous 0.1 M HNO_3 at a 5 mm diameter boron-doped diamond electrode ('+' indicates zero current).

of 1 mM $AgNO_3$ in aqueous 0.1 M HNO_3 at the surface treated boron-doped diamond electrode. On the first forward scan starting from +0.7 V *vs.* SCE to negative potentials the nucleation process starts at *ca.* 0.0 V *vs.* SCE followed by growth at more negative potentials. On the reverse scan a characteristic stripping response is observed indicative for dissolution of the metallic silver into solution. These observations are in accord with a recent study by Vinokur *et al.*[4] A closer look at the stripping peak reveals an asymmetric tailing indicating that the dissolution is slow and not complete. The second and third scan show a reduction peak at a significantly more positive potential in agreement with silver growth on the silver nuclei already present from the previous scan. The silver remaining on the diamond surface after the stripping process could also be verified by SEM and XPS measurements.[5] This incomplete oxidation of deposits on diamond has been reported for Ag[4,5] and Pb[6,7] but is not yet fully understood.

After recording the cyclic voltammograms, silver was deposited on the electron beam treated diamond surface from a solution of 1 mM $AgNO_3$ in aqueous 0.1 M HNO_3 by applying a potential of $E = +0.17$ V *vs.* SCE [Fig. 1(a) and (b)] and of $E = -0.3$ V *vs.* SCE (not shown) for periods of 3 min. The SEM image clearly shows that there is a high density of silver deposition in the unexposed area while in the darker electron irradiated area hardly any deposition occurred. However, when the deposition potential was set to more negative potentials, silver deposition was detected also in the areas exposed to the electron beam. Fig. 1(b) shows an SEM image which reveals a dark *ca.* 200 μm^2 irradiated area on a single (100) crystallite face without any silver deposition. The selectivity of the electron induced surface modification is such that even single diamond crystallites may be patterned and partly covered with silver. Hydrogenating highly resistive non-doped diamond is known to induce p-type surface conductivity.[8] However, the diamond samples are highly boron-doped making it very conductive and therefore, it can be assumed that the observed effect is a surface effect, and not a localised change in (surface) conductivity. A possibly related patterning effect has been observed after photo-treatment and electro-deposition of copper.[9]

The present study shows that diamond surfaces can be modified selectively and with high spatial resolution using a focussed electron beam and that metallic silver can be selectively deposited on the unexposed diamond surface. It is proposed that electron irradiation desorbs hydrogen, oxygen, and impurities from the as grown diamond surface yielding a surface of more positive electron affinity and lower activity towards silver nucleation and growth. It is widely accepted that oxygen functionalities play an important role in the surface activity of diamond electrodes. The selectivity towards the metal deposition can be improved by optimising the doses of electron irradiation and hence the level of dehydrogenation. Even the surface structure can be manipulated[2] to give hydrogen rich (1 × 1), hydrogen poor (1 × 1), hydrogen poor (2 × 1), or hydrogen free reconstructed (2 × 1) by controlling the level of dehydrogenation and the electron affinity may be fine tuned between $\chi = -1.27$ eV and +0.40 eV.

In conclusion, the electron stimulated modification of diamond surfaces may offer potential benefits in a wide range of applications, such as selective metal deposition, fabrication of microelectrodes and sensors, cold cathodes, and patterned field emitters.

Notes and references

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