

Journal of Korean Institute of surface Engineering  
Vol. 32, No. 3, Jun., 1999

# PHOTOELECTRODEPOSITION OF COPPER ON BORON-DOPED DIAMOND FILMS: ITS APPLICATION TO CONDUCTIVE PATTERN FORMING ON DIAMOND AND DIAMOND PHOTOGRAPHIC PHENOMENON

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## Abstract

Photoelectrodeposition of copper on semiconductive B-doped diamond films was investigated. There are clear morphology differences between photodeposited copper and electrodeposited copper. Photoelectrodeposition proceeded as uniform 2-dimensional growth. On the other hand electrodeposition proceeded as scarce random deposition. By applying this effect we have succeeded in forming a conductive pattern on semiconductive B-doped diamond with the aid of a photo-mask. And it was suggested that the surface reforming caused by photoelectrochemical process could be easily detected by the following metal (copper) deposition method, which is demonstrated as "Diamond photographic phenomenon".

*Key words* : B-doped diamond, copper, electrodeposition, photoelectrodeposition.

## 1. INTRODUCTION

Diamond is a well-known material for its hardness and its high thermal conductivity. So recently it was applied as a heat sink material for semiconductor LASER. In future such a unique characterized diamond films will be widely applied to the electronics fields. Diamond thin film could be easily obtained by microwave plasma assisted chemical vapor deposition (CVD). Thus prepared diamond films is highly insulating. But Fujishima et al have already succeeded in obtaining

conductive or semiconducting diamond films by mixing  $B_2O_3$  into ethanol and acetone as diamond source<sup>1)</sup>. Boron could be incorporated into diamond, and make it conductive. It is well known that the bandgap of diamond is 5.45eV, so excited electron has an extremely high reducing capacity. The purpose of this paper is the investigation of photoelectrodeposition of metals (e.g. Copper) on semiconductive B-doped diamond films. In addition we would like to present a quite amazing phenomena occurred on semiconductive B-doped diamond films, we called it as "diamond

photographic phenomenon". This will also introduced.

## 2. EXPERIMENTAL

The diamond thin films were grown by microwave plasma assisted CVD. Applied plasma power was 5kW and the inner pressure of the reaction chamber was 113–115 torr. The raw material for diamond was a mixture of acetone and methanol. The carrier gas was H<sub>2</sub> gas. The semiconductive films were grown on p-type Si(111) single crystal wafer until a thickness of 40 μm and doped with boron at an atomic concentration of 10 ppm B/C, (mixing ratio of B<sub>2</sub>O<sub>3</sub> to methanol and acetone). The substrate (Si) was entirely etched by mixed acid of conc. HF aq. and conc. HNO<sub>3</sub> aq. Thus obtained diamond was used as working electrodes or photoelectrodes, counter or reference was platinum coated titanium, SCE, respectively. The electrochemical measurements \*Cyclic voltammogram) were carried out using a potentiostat and a function generator. Before (40min) and during the experiment N<sub>2</sub> bubbling was carried out. Chemical etching for each substrate was performed by sulfuric acid: nitric

acid (1:1) solution for the purpose of etching surface sp<sup>2</sup> carbon. Experimental set up was shown in Fig. 1. The experiments of photodeposition were performed in a copper electrolyte composed of 1mM CuSO<sub>4</sub>, 50mM H<sub>2</sub>SO<sub>4</sub> aqueous solution. Crosscut diagram near the working electrode was shown in the inset figure of Fig. 1. The thickness of the electrolyte was ca. 3mm. The light source for excitation of semiconductive diamond was D<sub>2</sub> lamp. According to circumstances, two types of photomasks as shown in Fig.1 have been used, plate type (A) and grid type (B).

## 3. RESULTS AND DISCUSSION

Obtained photocurrent-potential curve and dark current-potential curve are shown in Fig. 2. The onset potential of the photocurrent was -0.12V vs. SCE. which did not accord to the doping level of Boron or the onset potential of the photocurrent previously reported. This discrepancy will be discussed later. In the potential region more negative than -300mV vs. SCE, the additional current accompanying hydrogen evolution reaction was observed. So we set the potential

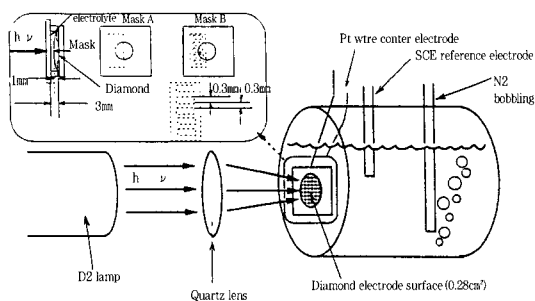


Fig. 1 Experimental set up for photoelectrochemical experiments.

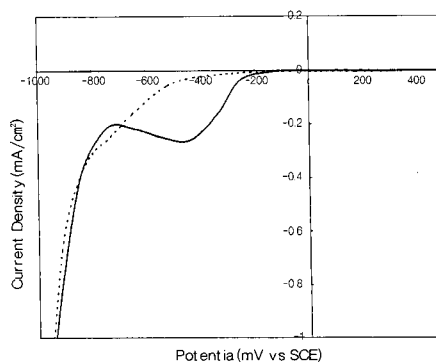


Fig. 2 Photocurrent-potential curve(—) and current-potential curve (---) obtained in 1mM CuSO<sub>4</sub>, 50mM H<sub>2</sub>SO<sub>4</sub> aq. sol.(Sweep rate:100m V/s)

for photodeposition or deposition as  $-250\text{mV}$  vs. SCE. First we have investigated the nature of photoelectrodeposition of copper on the semiconductive diamond. The FE-SEM photographs obtained for thus deposited diamond surfaces were shown in Fig. 3. The period of deposition or photodeposition was varied. Fig. 3 suggested that photodeposited copper dispersed uniformly on the diamond surfaces except for certain crystal planes (100), on the other hand electrodeposited copper on semiconductive diamond existed scarcely at grain boundaries or random sites. The effect of non-uniform metal electrodeposition on the dark is well known in the electrochemistry of semiconductors. It can be used to reveal structure defects in semiconductors. The non-uniformity is eliminated when the concentration of

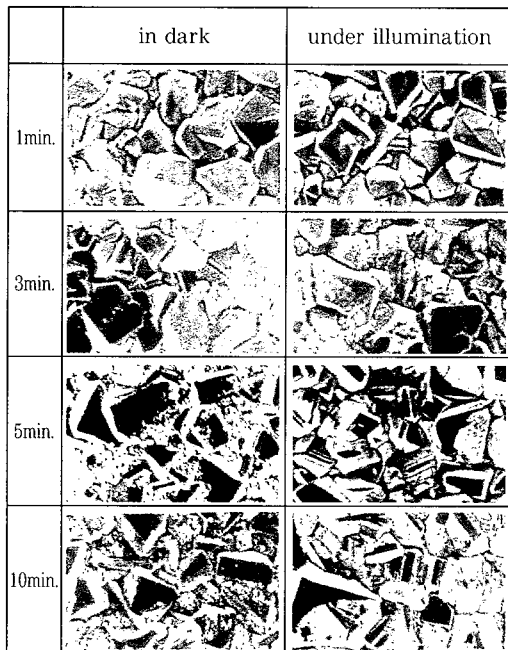


Fig. 3 FE-SEM photographs of the diamond surfaces deposited with copper electrochemically or photoelectrochemically after each deposition period.

photogenerated minority carriers exceeds that of the structure defects. From this point of view we tried to form the uniform conductive pattern of copper on semiconductive diamond. Near the diamond substrate the photo-mask was set at a distance of 1mm from the surface (See inset figure of Fig. 1). The potential of the electrode was maintained at  $-250\text{mV}$  vs SCE in the same electrolyte as above. Thus obtained surfaces (FE-SEM photograph) shown in Fig. 4 suggested that continual and uniform copper conductive pattern was observed clearly on the illuminated region. This study is quite important in the field of the electronic device, considering of the application of semiconductive diamond instead of silicon in future.

As a final topics we discovered unique characteristics of photocathodic reaction occurred on

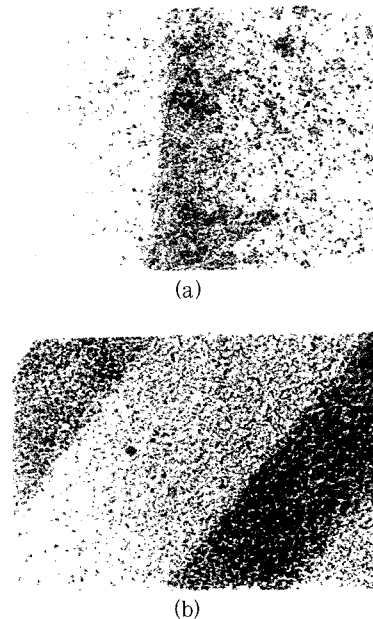


Fig. 4 FE-SEM photographs of the diamond surfaces partially deposited with copper photoelectrochemically. (a) half of the surface was photo-masked. (b) one part of the surface was photo-masked.

semiconductive diamond. First we deposited copper at  $-250\text{mV}$  vs SCE with using photo-mask under illumination, so that copper was deposited electrochemically on a half of the electrode, and on another half of the electrode copper was deposited photoelectrochemically. After that the surface showed similar tendency as mentioned above. (Fig. 5a-1, 2) After that thus deposited surface was first etched by aqua regia to dissolve the deposited copper, next washed by distilled water and finally etched by mixed acid of sulfuric acid : nitric acid (1:1) solution to dissolve surface  $\text{sp}^2$  carbon. FE-SEM photograph after these

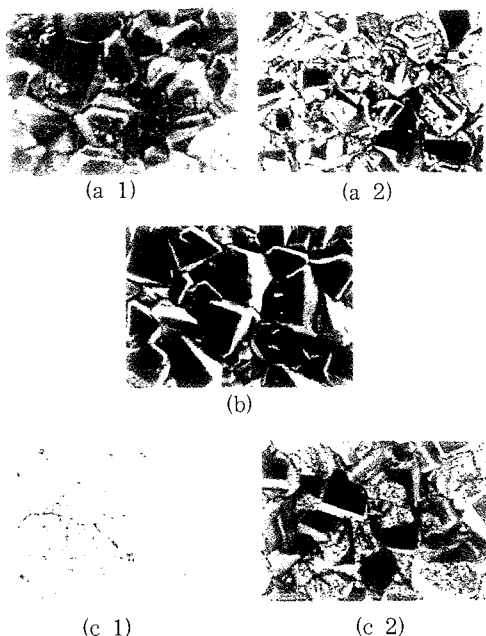


Fig. 5 PE-SEM photographs of the diamond surfaces after each treatment copper was deposited electrochemically on a half of the electrode(a-1), and on another half of the electrode copper was deposited photoelectrochemically(a-2), thus deposited surface was first etched by aqua regia. next washed with distilled water and finally etched by sulfuric acid : nitric acid (1:1) solution(b). copper was deposited on all region of the surface in dark(c-1,2)

etchings looked the same as the original diamond surface before deposition. (Fig. 5 b) But after that, copper was deposited on all region of the substrate at  $-250\text{mV}$  vs SCE in dark (not "photoelectrochemically"). FE-SEM photographs (Fig. 5 c-1, 2) after this deposition suggested that the feature of photoelectrochemical deposition as mentioned above was reproduced on the half of the electrode, where the photoelectrochemical deposition took place "before". We call it "diamond photographic phenomenon", from the analogy to the mechanism of the monochrome photograph. We investigated the origin of this phenomenon in detail. First the electrode was polarized at  $-250\text{mV}$  vs SCE in  $50\text{mM}$   $\text{H}_2\text{SO}_4$  aqueous solution. with using photo-mask under illumination. The photocurrent-potential or dark current-potential curves were shown in Fig. 6. As suggested by this figure, at  $-25\text{mV}$  vs. SCE in  $\text{H}_2\text{SO}_4$  aqueous solution, hydrogen was not evolved electrochemically on a half of the electrode (dark side) and on another half of the electrode (light side) hydrogen was evolved "photoelectrochemically". After that thus treated surface was washed by distilled water. FE-SEM photo-

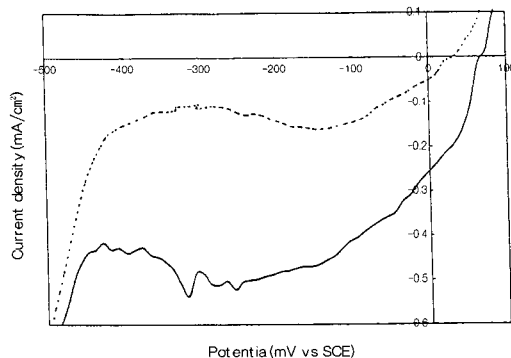


Fig. 6 Photocurrent-potential curve(—) and current potential curve(- -) obtained in  $50\text{mM}$   $\text{H}_2\text{SO}_4$  aq. sol.(Sweep rate:  $10\text{mV/s}$ )

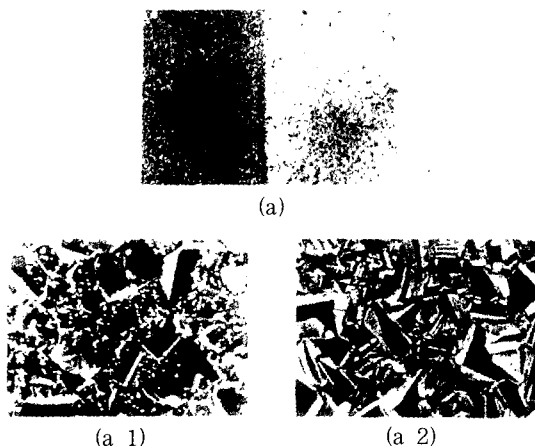


Fig. 7 FE-SEM Photographs of the diamond surface after each treatment, the diamond electrode was polarized at  $-250\text{mV}$  vs, SCE with the aid of photo-mask(Mask A in Fig. 1). As shown in Fig. 6 small amount of hydrogen was evolved electrochemically on a half of the electrode (dark side), and another half of the electrode (light side) hydrogen was evolved photoelectrochemically, thus treated surface was washed with distilled water, after these treatment we could not see any discrepancy between both side. Next copper was deposited on all region of the surface in darks(a). The surface (previously dark side a-1)(previously light side. a-2).

graph after this process looked the same as the original diamond surface. After that, copper was deposited on all region of the substrate at  $-250\text{mV}$  vs SCE in dark (not "photoelectrochemically") in  $1\text{mM}$   $\text{CuSO}_4$ ,  $50\text{mM}$   $\text{H}_2\text{SO}_4$  aqueous solution. FE-SEM photographs (Fig. 7) after this deposition suggested that continuous growth of

copper film occurred on the half of the electrode, where the photoelectrochemical evolution of hydrogen took place "before". On the other hands on another half of the electrode the deposition of copper could be scarcely observed as shown in Fig. 7(a-1). Considering above results the origin of "Diamond photographic effect" is in photoelectrochemical intercalation of hydrogen into diamond or surface reforming caused by photoelectrochemical evolution of hydrogen. Recently Bouamrane et al reported that underpotential deposition of Cu occurred on Boron-doped diamond thin films<sup>2)</sup>. They reported the possibility of intercalation of copper into diamond or alloying. Perhaps also in this case photoelectrochemically reduced hydrogen intercalates into diamond surface or reforms the surface, so thus resided or denatured hydrogen plays a role as a nucleus for electrodeposition. Anyhow we suggested that the surface reforming could be easily detected by the following metal (copper) deposition method, which is demonstrated as "Diamond photographic phenomenon".

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