doi:10.1017/S1431927612009646
Microsc. Microanal. 18 (Suppl 2), 2012

TEM observation of nitrogen-doped diamond films.

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There is great demand for devices that convert heat and solar energy to electrical energy. Diamond films that have been doped with nitrogen are proving to be promising materials for energy conversion applications. The high electric and thermal conductivity and negative electron affinity (NEA) of the hydrogen-terminated nitrogen-doped diamond enables high efficiency in thermionic emission [1,2], field emission [3] and secondary electron emission [4].

A thermionic energy converter consists of a hot emitter and a cold collector connected to a load and separated by vacuum. Electrons emitted from the surface reach the collector and so a voltage is generated. Of course, the efficiency of such a system with a heat source and a heat sink is limited by the efficiency of the Carnot cycle. The collector may be fabricated so that a photon beam passing through it illuminates the emitter. This design enables both thermionic and photoelectron emission. Conventional thermionic convertors are based on electron emission from flat metal surfaces at high temperatures, 2000K or more. This, and the bulky "cesiation" design [5], considerably limit the energy applications of such devices. Recent efforts have been concentrated on simplified operation and reduction of the work function of the converters and, therefore, of the operating temperature.

The use of H-terminated N-doped diamond films enables conversion at temperatures less than 1000K [1]. The H-termination results in NEA of the surface layer [2], i.e. the vacuum level is below the conduction band minimum (CBM). The n-type doping creates donor levels in the diamond's band gap close to the CBM, which considerably lowers the work function. The upward band bending, observed at the surface of the diamond film, is obviated by introducing an intermediate N-doped ultra nano-crystalline diamond (UNCD) layer between the film and the substrate [1]. As result a less than 1.5 eV effective work function is obtained and thermionic emission below 600K is reported in a "noncesiated" convertor [6].

The large band gap makes diamond transparent for visible light. Nevertheless, visible light photo emission (PE) combined with thermionic emission (TE) from H-terminated N-doped diamond film emitters is observed [6]. The PE may be understood in terms of a 3-step process: substrate electrons are excited above the interface barrier, transported to the surface with NEA, and finally emitted. Clearly, the TE and PE characteristics are closely related to the emitter's microstructure. For instance, sp^2 bonds present in UNCD grains are believed to mitigate the upward band bending [1]. This study reports TEM characterization of H-terminated N-doped diamond films grown on Mo and B-doped Si.

The films have been synthesized with plasma-assisted chemical vapor deposition. The procedures consist of (i) seeding by ultrasonication of the substrate in a nano-diamond slurry and rinsing, (ii) vapor deposition of the nitrogen incorporated UNCD layer in microwave plasma while maintaining a certain temperature of the substrate, (iii) changing the vapor and plasma parameters for N-doped diamond layer deposition and exposing the surface to the hydrogen plasma to obtain the NEA characteristic of the emitter.

A PE threshold of 2.3 eV is observed in the film with Mo substrate (Fig.1 right). This suggests that the Schottky barrier of the film-substrate interface is higher than the surface work function. However, other Mo-based samples showed the same threshold for both PE and TE (1.5 eV). Grain boundary and interface scattering limit the electron transport in the emitter. So it can be concluded that such properties as graininess of the diamond film, grain size and interface roughness that vary from sample to sample may play an important role in understanding the barrier structure of emitters and observed characteristics. These properties can be quantified by means of TEM images (Fig.1). Grains of 2 nm to 5 nm in size are visible in Fig. 1 (right) near the rough Mo interface, whereas the film on the left image seems to be amorphous. A PE and TE threshold of 1.7 eV is detected in the film with Si substrate (Fig.1 left), which may be attributed to the surface work function which is higher than the Si-SiC-C heterojunction barrier. The narrow SiC layer, which was not synthesized intentionally, is distinguishable on the left image. Note the higher quality of the interface in the Si-based sample (left) compared to the Mo-based sample (right). This, presumably, is the reason for a low interface barrier.

The extent of disorder in the diamond layers may be important. Conventional imaging and diffraction techniques are not sensitive to the medium range order (MRO), especially from 1 to 2 nm. For this reason Fluctuation Electron Microscopy (FEM) characterization of the samples described in this study will be useful [7]. In particular, regions of the diamond film that look amorphous on TEM images (Fig.1 left) are good candidates for FEM. We also plan to conduct an interferometric FEM with the Nion UltraSTEM 100 aberration corrected microscope to quantify MRO in the H-terminated N-doped diamond films and reveal its role in emitter characteristics.

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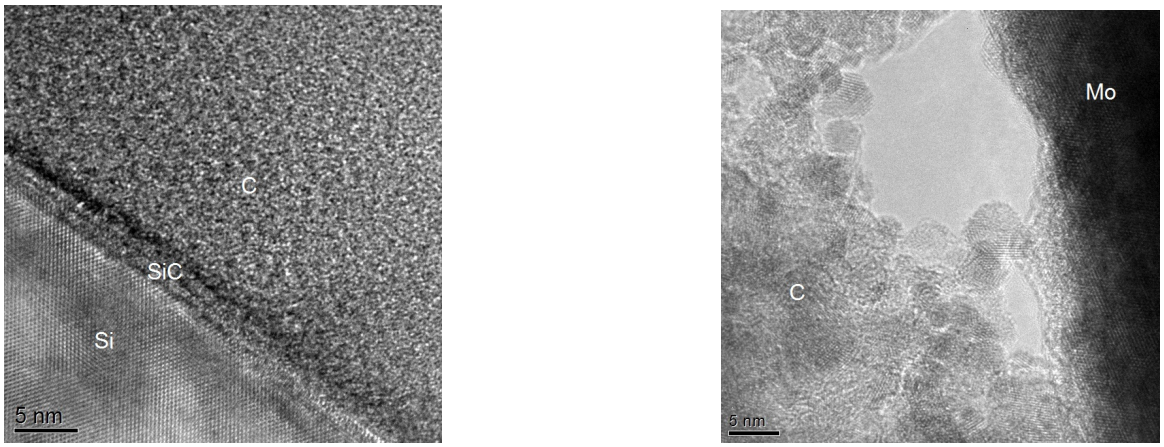

FIG 1. Cross sectional view TEM images of the interface of the UNCD layer and the substrate. JEOL 2010F, 200 keV. Left: B-doped Si substrate. Prepared by dimpling and ion milling in PIPS. Right: Mo substrate. Prepared by FIB in situ lift out.