

Electronic Supplementary Information (ESI)

2-dimensional micro-network of boron-doped diamond film : fabrication and electrochemical sensing application

Daibing Luo,^{*a,b} Liangzhuan Wu^a and Jinfang Zhi^{*a}

^a *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing
100190, China; E-mail: luodb@scu.edu.cn; zhi-mail@mail.ipc.ac.cn*

^b *Analytical & Testing Center, Sichuan University, Chengdu 610064, China*

This supporting information covers 4 pages, including reagents, instrumentation, and the preparation procedures of the boron-doped diamond micro-network (BDDMN) film.

Reagents

p-type silicon wafers (100) were obtained from Shin-Etsu Chemical Co., Ltd (Japan). SiO₂/Si wafers and photo masks were made in School of Software and Microelectronics of Peking University. UA (uric acid) was purchased from Aldrich. Photoresist was obtained from micro resist technology GmbH (Germany). Diamond nanoparticles were purchased from Beijing Guoruisheng technology Co., Ltd. All chemicals were analytical grade or better. Double distilled ultra-pure water (>18MΩ cm) was used for all solutions preparation.

Apparatus

The HFCVD (hot filament chemical vapor deposition) system was purchased from Shanghai JiaoYou Diamond Coating Co., Ltd. The scanning electron microscopy (SEM) was performed using a Hitachi Ultra-high-Resolution S-4300 microscope. The Raman spectroscopy was obtained using a Renishaw 1000 Raman spectrometer (Renishaw Ltd., UK).

Electrochemical measurements

Electrochemical measurements were made using a 263 A potentiostat/galvanostat (Princeton, USA) controlled by a PC. A three-electrode system consisting of a working electrode (BDDMN, BDD (boron-doped diamond)), a saturated calomel electrode (SCE) reference electrode, and a Pt auxiliary electrode was connected to the workstation. All measurements were taken at room temperature under nitrogen protection. A normal planer BDD electrode prepared under the same conditions from HFCVD works for comparison. Before use, the working electrodes (BDDMN, BDD) were washed under ultrasonication in 2-propanol followed by ultra-pure water for 10 min, respectively. The electrode geometric surface area exposed to the solution was 0.1cm².

Synthesis of SiNWs (Silicon nanowires)

SiNWs were prepared by Electroless metal deposition (EMD) method (K. Q. Peng,

Y. J. Yan, S. P. Gao and J. Zhu, *Adv. Funct. Mater.*, 2003, **13**, 127-132). The synthesis of SiNWs was carried out in a Teflon-lined stainless-steel autoclave. A *p*-type silicon (100) wafer was cleaned ultrasonically in acetone, ethanol and pure water for 10min, respectively. The cleaned silicon wafer was immersed in a mixture of 4.6 M HF and 0.02 M AgNO₃ aqueous solutions with equal volume. Then, the autoclave was sealed and put into an oven immediately. After etching for 40 min at 50 °C, the silicon wafer wrapped with a thick gray film was taken out from the autoclave. The sample was dipped in 30 wt% HNO₃ aqueous solution for 60 s to remove the capped silver. Finally, the sample was rinsed with deionized water and ethanol, dried in air and sent to further analysis.

Fabrication of BDDMN

A droplet of silicon nanowires suspension in ethanol was deposited on the SiO₂ surface of the SiO₂/Si wafer. After ethanol evaporation, a standard photolithography process was performed. In this process, 0.5 mg of diamond nanoparticles was firstly dispersed reasonably in 2 mL of photoresist. This step ensured desired and uniform HFCVD diamond growth. The photoresist mixed with diamond nanoparticles was sputtered on the surface of the SiO₂/Si wafer using spin coater with 3000 rpm for 1 min, and this coated wafer was baked at 60 °C for 30 min in an incubator. After that, conventional photolithography and wet etching was performed with the photo mask defining the patterned area. The photoresist-coated surface of the SiO₂/Si wafer was put under the photo mask and exposed in ultraviolet ray (315 nm) irradiation for 1 min. By soaking the wafer in 0.5 % NaOH solution, the region of the photoresist exposed to ultraviolet rays was removed and the residual pattern was obtained on the surface of the SiO₂/Si wafer.

During the HFCVD process, acetone solution containing trimethyl borate (0.5% atoms ratio) was used as the carbon source. The carbon source/H₂ flow ratio was 50:200 sccm (the approximate atom ratio of B:C:H was 1:60:200) and the growth duration was 60 min. The bias voltage was set at 4.5 V. The substrate was heated by 4 Tantalum wires with an ac power supply at a voltage of 20 V and the current of 75 A.

The deposition power was kept at about 1500 W and the pressure was maintained at 1 kPa. In this process, the photoresist was decomposed under low pressure and high temperature, leaving the diamond nanoparticles as the nucleation seeds. Diamond nucleation was formed very fast on the seeds and the SiNWs, and the growth began from these nuclei on the SiO₂ surface.