



Short communication

Aligned Pt-diamond core-shell nanowires for electrochemical catalysis

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ABSTRACT

Heavily boron-doped diamond electrode has been applied as a robust substrate for Pt based catalyst. However, by simply applying a planar electrode the effective surface area of the catalyst is limited. In this article we for the first time prepared vertically aligned Pt-diamond core-shell nanowires electrode in a convenient and scalable method (up to 6-inch wafer size). The diamond nanowires are first fabricated with reactive ion etching with metal nanoparticles as etching masks. The following Pt deposition was achieved by DC sputtering. Different amounts of Pt were coated on to the nanowires and the morphology of the core-shell wires is characterized by SEM and TEM. The catalytic oxygen/hydrogen adsorption/desorption response are characterized by cyclic voltammetry. The results show that the active Pt surface area is 23 times higher than a planar Pt electrode, and 4.3 times higher than previously reported on Pt nanoparticles on diamond by electro-deposition. Moreover, this highly active surface is stable even after 1000 full surface oxidation and reduction cycles.

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1. Introduction

Boron-doped diamond (BDD) electrode has been proved to be an ideal substrate for the deposition of metal catalysts due to its excellent chemical, physical stability and conductivity [1–3]. Particularly, the deposition of platinum on diamond has been widely investigated [2–5]. Many important issues such as particle density [2], reactivity [5], as well as particle-diamond adhesion [3] are dealt with in these studies. However, for a planar electrode, even if it is fully covered by a dense layer of Pt particles, the active area enlargement is still limited to around 4 times [2].

For traditional Pt/C catalyst, porous carbon is used to provide sufficient surface area [6], and the same approach can also be applied for diamond based catalysts. With diamond surface nanostructuring techniques, aligned diamond nanowires can be conveniently fabricated with specific surface area one magnitude higher than planar electrodes [7]. These wires have proved to be good surface-enhanced substrates for applications such as catalysis and sensors [8–10]. However, for catalysts there are only very limited reports, and in these reports the metal catalyst only covers a very small area because of fabrication methods [11,12]. As a result, the total active area is still not high.

In this article, we tried to enhance the active surface area of Pt/diamond electrode by using diamond nanowires fully covered by Pt nanoparticles. The highly conductive BDD is synthesized using microwave chemical vapor deposition (MWCVD) method; BDD nanowires are fabricated using inductance coupled plasma (ICP) etching with self-organized metal nanoparticles as etching mask. 1–3 nm of Pt is coated via direct current (DC) sputtering. All these techniques are easy

to scale up to a 6-inch level. SEM (scanning electron microscopy) and TEM (transmission electron microscopy) images show that the Pt-diamond composite forms a core-shell structure with Pt uniformly covering the nanowires. The performance of such an electrode is characterized by electrochemistry techniques. The results show that the electrode is highly active and stable and power density is one magnitude higher than current literature.

2. Experimental

2.1. Fabrication

BDD substrate for nanowires is synthesis with a MWCVD method on Si (100) substrate. Before BDD growth the silicon wafer was seeded with a special nanodiamond seeding process described elsewhere [13]. To realize boron doping trimethylborane was added to the H₂/CH₄ mixture. The growth parameters are: 2% methane in hydrogen, microwave power: 3200 W, gas pressure: 50 mbar and substrate temperature: 750 ± 10 °C. Boron concentration was set to [B]/[C] = 4000 ppm. The overgrowth duration was 50 h which resulted in a film thickness of ~10 μm. The diamond quality is characterized by Raman Spectroscopy (Fig. 1a). The BDD is of low sp² content and the boron concentration was measured to be above 10²¹ cm⁻³ [14].

After BDD growth, nanowires are fabricated with a top-down ICP etching process [15]. A 4-nm-thick titanium layer is deposited via DC sputtering on BDD surface, followed by thermal de-wetting at 1000 °C for 1 min to form metal nanoparticles on BDD surface. The sample is then transferred to an ICP etching process with: 1200 W ICP power, 300 W high frequency (HF) power, and –200 V bias voltage, under a 50 SCCM O₂ flow. The etching duration was 5 min. After etching the

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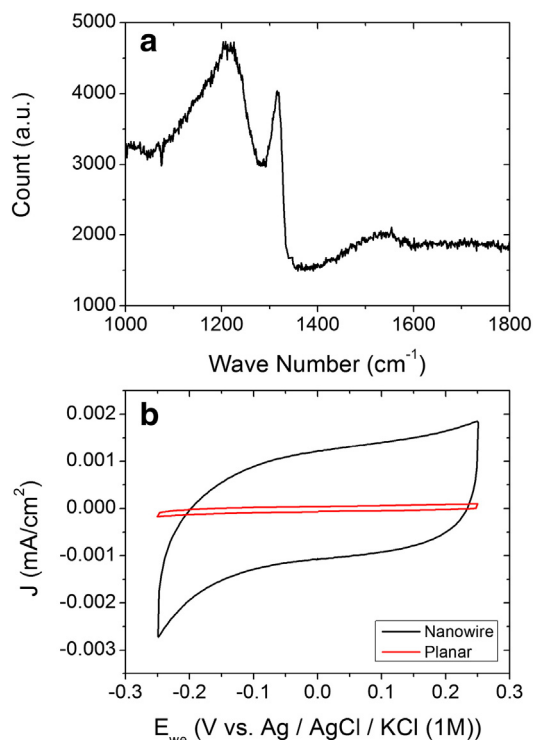


Fig. 1. (a) Raman spectroscopy of BDD wafer; (b) cyclic voltammetry between -0.25 and 0.25 V at scan rate of 5 mV/s in 0.5 M NaClO_4 solution showing enlarged capacitive current of nanowires.

nanowires are cleaned by a mixture of 98% H_2SO_4 and 65% HNO_3 ($3:1$) at 200°C . The surface enlargement of the nanowire forest was measured from capacitive background current of cyclic voltammetry described previously [15] as 19.2 times (Fig. 1b).

Pt with nominal thicknesses of 20, 40, and 60 nm are deposited on the cleaned nanowire samples via direct current (DC) sputtering. The Ar pressure was 5×10^{-3} mbar, deposition voltage was 500 V and current was 0.6 A. The Pt mass calculated from the deposition thickness for the three samples are 42.9, 85.8, and $128.7 \mu\text{g}/\text{cm}^2$, respectively. All the processes are performed on a 3-inch wafer with the possibility to be expanded to a 6-inch scale.

2.2. Characterization

The morphology of samples was characterized via SEM (Hitachi S-4500II, Japan) and Transmission electron microscopy (Zeiss LEO 912 Omega, Germany). Electrochemical experiments were conducted with a VMP-3 Biologic Multi-channel Potentiostat (Biological Inc., France). A standard three-electrode system was applied with an Ag/AgCl (in 1 M KCl) reference electrode and Pt counter electrodes. Working electrodes were contacted through a Ti/Pt/Au (20/60/200 nm) metal contact. The geometric area of the working electrode is 0.5 cm^2 . All the current densities discussed later on have been normalized by this area. 3 samples from wafer center, between center and edge and wafer edge are tested to give averaged results. $2 \text{ M H}_2\text{SO}_4$ is used as supporting electrolyte for all the electrochemical measurements. In order to avoid the dissolved oxygen in the electrolyte, all the electrochemistry characterizations have been done in a N_2 glove box.

3. Results and discussion

Fig. 2(a) shows the SEM image of diamond nanowires. The wires have tapered shapes with sharp tips. This is a preferred shape for the following metal deposition to achieve a high coverage. For the sample with 20 nm Pt deposition (PtDia20) (Fig. 2b), the wires' surface becomes

rough, showing metal coverage. As more Pt is deposited (Fig. 2c and d) the wires get thicker and become corrugated nanorods. The coverage was uniform without obvious difference between the top and bottom part of the wires. Although the samples with total amounts of 40 nm Pt deposition and 60 nm Pt deposition (PtDia40 and PtDia60) look similar, as the metal layer gets thicker it is expected that the neighboring wires start to agglomerate and the space between wires to be filled by Pt. Therefore, an optimized metal thickness needs to be found out.

The fine structures of these wires were further characterized by TEM (Fig. 3). A uniform coverage of nanoparticles from top to bottom of the wires is detected in all the three samples. Interestingly, the Pt deposited on diamond wire forms self-assembled into nanoparticles with a typical size of less than 10 nm. This process is believed to minimize the overall interfacial energy, as is described by theory of equilibrium shape of supported nanoparticles [16]. We also confirmed that for PtDia20 sample, the coverage is not complete. With more Pt deposition, PtDia40 and PtDia60 show a full coverage of nanoparticles. However, the wires also start to agglomerate. Fig. 3(b) and (c) actually shows a bunch of wires covered by Pt nanoparticles. Therefore, PtDia40 should be the optimized deposition condition.

Electrochemical activities of these samples confirmed this point. The cyclic voltammetry of all the samples in a potential window of 1.2 V is performed at 100 mV/s; planar Pt samples are also measured for comparison (Fig. 4a). For all the samples, hydrogen adsorption/desorption happened at potentials lower than 0.2 V while Pt surface oxidation happened from 0.6 V to 1.0 V. The surface reduction appeared as a broad peak from 0.9 to 0.1 V. It is worth noticing that for PtDia60, the shape of the hydrogen desorption peak change, and a distinct peak appears at -0 V vs Ag/AgCl. Previous studies on H-desorption peaks show that this peak is attributed to Pt (100) facets [5,17]. Therefore, an evolution of Pt particle shape happened during the Pt deposition. For Pt nanoparticles, (111) surface has the lowest surface energy [18], and this is the case for small amount Pt depositions (PtDia20 and 40). For a (111)-dominating configuration of nanoparticle one can refer to a pyramid, with its bottom in contact with diamond. As more Pt was deposited, the pyramid will grow. If the diamond-Pt interface has a very low interfacial energy (see the last paragraph) the pyramid will expand in size rather than in height. In this way, the pyramid will grow into a truncated one, i.e. (100) facet will appear at the top. However to confirm this hypothesis atomic resolution TEM is needed, and this work is now under investigation.

The Pt surface area can be calculated from the hydrogen desorption peak area Q_H in cyclic voltammetry (Fig. 4b). To measure the active Pt surface area, the standard Q_H value $0.21 \text{ mC}/\text{cm}^2$ is used [6]. A higher Q_H represents a larger surface area. For PtDia20, because the surface is not fully covered by Pt, the Q_H value didn't reach the maximum. The largest hydrogen desorption signal is from PtDia40 ($4.82 \text{ mC}/\text{cm}^2$) which corresponds to 23 times of a planar platinum electrode. This is slightly larger than the surface enlargement of the diamond nanowire forest of 19.2 times probably due to the rough metal surface. Moreover, this value is ~ 20 times higher than what we achieved previously with direct electrochemical deposition method ($0.25 \text{ mC}/\text{cm}^2$), and is ~ 4 times higher than the best value ($0.91 \text{ mC}/\text{cm}^2$) we achieved previously [2]. Because of the wire agglomeration, the surface is smaller than twice of PtDia20. As more Pt is deposited, the problem of agglomeration is also more severe. For PtDia60, the surface area is even smaller than PtDia40. This trend leads to a decrease in specific area of Pt (SA), which is calculated using:

$$SA = \frac{Q_H/0.21}{M_{\text{Pt}}} \quad (1)$$

where M_{Pt} is the mass of Pt loading on each sample (42.9 , 85.8 , and $128.7 \mu\text{g}/\text{cm}^2$ for DiaPt20, 40 and 60, respectively). The results are plotted in Fig. 3(b). The highest number of $33 \text{ m}^2/\text{g}$ was achieved on

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