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Preparation of platinum nanoparticles on *n*-GaN(0001) substrate by means of electrodeposition

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ABSTRACT

Nanoparticles of platinum (Pt) were directly prepared on *n*-GaN(0001) by a potentiostatic electrodeposition in 0.5 M H_2SO_4 + 8 mM H_2PtCl_6 solution and fully characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray analysis (EDAX). The as-deposited nanoparticles, whose morphology and size were dependent on the applied potential and time, were made of platinum. The real surface area and catalytic properties of Pt nanoparticles prepared at different potentials were estimated by cyclic voltammetry in 0.5 M H_2SO_4 and by chronoamperometry in 0.5 M H_2SO_4 + 0.2 M CH_3OH solutions, respectively. The maximum of real surface area and the best catalytic activity of Pt nanoparticles were obtained at the potential of −0.7 V.

1. Introduction

Gallium nitride (GaN) is a direct band-gap semiconductor with a wide band-gap of 3.4 eV at room temperature [1,2]. The GaN-based materials have been extensively used in various optoelectronic devices, such as light emitting diodes, lasers, transistors, and ultraviolet detectors [3–5]. Besides applications in physics field, there is also an increasing interest in chemistry field due to their excellent chemical stability and unique optoelectronic properties. For instance, platinum (Pt) nanoparticle-modified GaN was found to have potential applications in catalysis and sensors. Schäfer et al. revealed a large influence of GaN on the chemical composition and oxygen affinity of supported Pt nanoparticles under X-ray irradiation. Polyvinylpyrrolindone-capped Pt nanoparticles were prepared by a polyol process [6]. Zdansky developed very sensitive and temporally stable hydrogen sensors, in which colloidal Pt nanoparticles were prepared by reducing aqueous solutions of metal salts in reverse micelles with sodium di-2-ethylhexylsulfosuccinate surfactant and electrophoretically deposited onto GaN [7]. It is to be noted that the Pt nanoparticles in the above studies were synthesized in the reduction chemical process and transferred to the substrates. Additional impurities might be included during their transfer. Therefore, the methods that can form Pt nanoparticles directly on GaN are highly expected. On the other hand, the electrodeposition of Pt nanoparticles has been studied on various electrodes, such as glassy carbon, indium tin oxide, carbon nanotubes, *n*-type silicon, and boron-doped diamond [8–12].

Herein, we report for the first time the electrodeposition of Pt nanoparticles on a surface of *n*-GaN(0001) via a direct potentiostatic transient process in 0.5 M H_2SO_4 + 8 mM H_2PtCl_6 solution. To the best of our knowledge, no reports have described the preparation of metal nanoparticles (including Pt) on GaN single-crystal substrate by electrodeposition. The as-deposited nanoparticles were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray analysis (EDAX). The real surface area and catalytic activity of Pt nanoparticles prepared at different deposition are estimated by cyclic voltammetry in 0.5 M H_2SO_4, 0.5 M H_2SO_4 + 0.2 M CH_3OH solutions, and chronoamperometry in 0.5 M H_2SO_4 + 0.2 M CH_3OH solutions, respectively.

2. Experimental

Single-crystal *n*-GaN(0001) substrates were 7 mm × 5 mm, Si doped *n*-type, and grown by hydride vapor phase epitaxy on sapphire. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Sigma–Aldrich Co., methanol was purchased from Alfa Aesar. Ethanol, acetone, and sulfuric acid (98%) were purchased from Shanghai Chemicals Co., deionized (DI) water (>18.2 MΩ) was used to prepare all aqueous solutions and for rinsing unless otherwise noted. The GaN substrates were ultrasonicated in acetone, ethanol, and DI water for 15 min, respectively.

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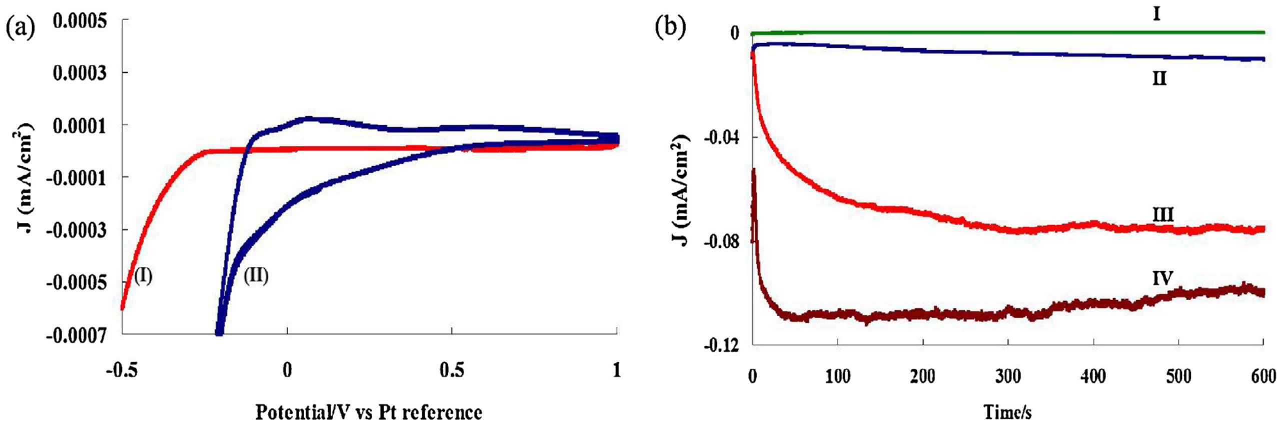

Fig. 1. (a) Cyclic voltammograms of *n*-GaN(0001) in 0.5 M H_2SO_4 (line I) and 0.5 M H_2SO_4 + 8 mM H_2PtCl_6 (line II). The scan rate was 0.1 V/s. (b) Potentiostatic current density–time transient for Pt electrodeposition on *n*-GaN(0001) in 0.5 M H_2SO_4 + 8 mM H_2PtCl_6. The applied potentials were (I) −0.3 V, (II) −0.5 V, (III) −0.7 V, and (IV) −0.9 V.

For Ohmic contact, an indium dot was melted onto a corner of GaN. The GaN substrate with indium dot, Pt wire, and Pt plate were used as working reference, and counter electrodes, respectively. Electrochemical operation was carried out by a potentiostat (CHI660D, Shanghai ChenHua Co.). The Pt nanoparticles were prepared by a potentiostatic electrodeposition in 0.5 M H_2SO_4 + 8 mM H_2PtCl_6. The as-electrodeposited Pt nanoparticles were fully characterized by SEM (Hitachi S4800), XRD (D8 Advance), and EDAX (Quanta 400 FEG). The real surface area and mass activity of Pt nanoparticles on GaN are estimated by cyclic voltammetry in 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 0.2 M methanol, respectively.

3. Results and discussion

Fig. 1a shows typical cyclic voltammograms (CVs) of *n*-GaN(0001) substrate in 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 8 mM H_2PtCl_6. It can be seen that the cathodic current decreases sharply at about −0.25 V in 0.5 M H_2SO_4. This is due to the evolution of hydrogen. With the addition of H_2PtCl_6, the onset of cathodic current changes positively to about 0.5 V. This is significantly different from that in 0.5 M H_2SO_4 and indicates the occurrence of Pt electrodeposition. Fig. 1b shows a set of current density–time transient curves in the potential range from −0.3 to −0.9 V. The current increases sharply at the beginning of each curve, then decreases rapidly, and finally becomes level. The above three processes are associated with the charging of the electrical double layer, the generation of Pt nuclei, and the growth of Pt nanoparticles on *n*-GaN(0001) substrate, respectively. Moreover, the level of current density and the time for leveling are found to decrease with the applied potentials. The loading mass of the Pt nanoparticles deposited at different potentials on GaN substrates is estimated from the electrical charge by integration of *I*–*t* curves, assuming that $[PtCl_6]^{2-}$ anions are completely reduced to the Pt atoms.

Fig. 2 shows SEM images of Pt nanoparticles prepared on *n*-GaN(0001) substrate with different deposition potentials. The Pt nanoparticles can be recognized as bright dots which locate randomly on *n*-GaN(0001) surface. At a potential of −0.3 V, the Pt nanoparticles are sparsely deposited, and their average sizes are tens of nanometers (Fig. 2a). The inset in Fig. 2a shows a high-magnification SEM image of a single Pt nanoparticle. It is clear that each particle is composed of a number of smaller ones, which are several nanometers in size, randomly-oriented, and connected with each other. As the potential decreases, the deposited Pt nanoparticles become not only larger in diameter, up to hundreds of nanometers, but also denser on GaN(0001) substrate (Fig. 2b and c). From the potential of −0.7 V, the Pt nanoparticles are close to overlap. Finally, some of Pt nanoparticles start to overlap (Fig. 2d), and form some small pieces of Pt clusters at a potential of −0.9 V. Similar results have been observed in previous studies of the electro deposition of copper on GC electrode, surface morphology of copper shifts from particles at high potentials to mirror-like films at low potentials because of the nanoparticles of Cu overlap [13].

To understand their crystal structures, the XRD spectrum of nanoparticles (Fig. 3a) has been recorded. The spectrum reveals three characteristic peaks at 40.1 °C, 46.2 °C, and 67 °C. These peaks are comparable with those of the face-centered cubic structures of Pt described in the literatures [14,15]. Similarly, they can be indexed to the (111), (200), and (220) planes of Pt, respectively. Fig. 3b shows the EDAX spectrum of nanoparticles deposited on *n*-GaN(0001) substrate. Besides peaks of elements of nitrogen and gallium, only the peak of platinum element is observed in the spectrum. Therefore, it is concluded that the as-electrodeposited nanoparticles are made purely of platinum.

The surface area of the Pt nanoparticles prepared at different potentials on *n*-GaN(0001) substrate is compared by conducting CVs in 0.5 M H_2SO_4. As shown in Fig. 3c, the three main peaks in CVs are comparable to those of Pt deposited on GC and metal electrodes in previous work [16,17]. The area of peak A is related to hydrogen desorption from the surface of Pt nanoparticles, and the area of the peak can be used for the estimation of the real surface area of Pt nanoparticles by formula of $A_r = Q/Q_{ref}Q$ is the electrical charge of

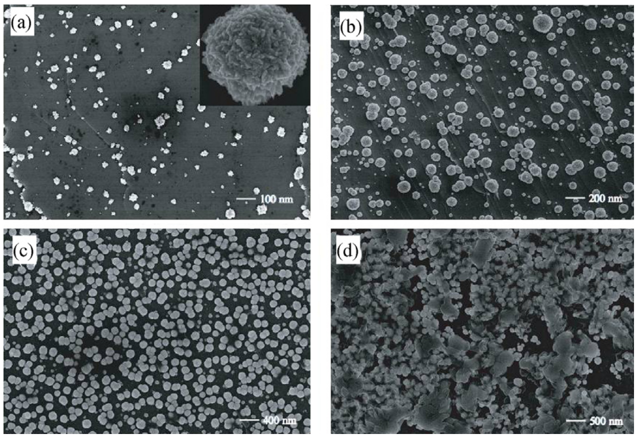

Fig. 2. SEM images of Pt nanopaticles prepared on *n*-GaN(0001). The deposition time was 20 min. The applied potentials were: (a) −0.3 V, (b) −0.5 V, (c) −0.7 V, and (d) −0.9 V.