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A novel method for the synthesis of Au nanoparticles incorporated amorphous hydrogenated carbon films

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Abstract

In this communication we report a novel electrochemical route for the preparation of Au nanoparticles incorporated a-C:H films on single crystal silicon substrates by choosing methanol as carbon source and Au nanoparticles as dopant. The morphology, composition and structure of the film have been investigated and the results show that the film obtained in our method is a hydrogenated diamond-like carbon film and zero-valence Au nanoparticles are stable and well-dispersed into the amorphous carbon matrix with unchanged size. It is simplified to achieve the co-deposition of carbon and metal by using metal nanoparticles rather than the metal salt solution as the dopant. The incorporation of Au nanoparticles in the carbon matrix can drastically decrease the resistivity and convert a-C:H films from insulator to semiconductor easily. The growth mechanisms of the Au-DLC films are also discussed.

Keywords: Carbon films; Electrochemical deposition; Metal-doped a-C:H film; Transmission electron microscopy; Microstructure

1. Introduction

Amorphous hydrogenated carbon (a-C:H) films are considered as promising materials with unique properties of extremely high hardness, high thermal conductivity, optical transparency, chemical inertness, high electrical insulation, high wear resistance, etc [1]. Although a-C:H films exhibit many desirable characteristics for several applications, their properties can be further modified or improved by doping with other elements. For example, metal incorporated a-C:H films (Me-DLC) with properties of both a-C:H and metal carbides have been shown to have low friction coefficient, low abrasive wear rate and good adhesion to metal substrates [2–4]. Moreover, doping a-C:H films with metals could alter the electrical property even with a very small metal concentration [5,6]. Recently, metal containing a-C:H films have been interesting as nanocomposite films with microstructures comprising of metal nanocrystalline grains in an amorphous carbon matrix [7]. With metal nanoparticles incorporated into a-C:H matrix, not only are the metal particles stabilized and prevented from agglomeration, but also have the metal-carbon films novel multifunction in electronics, optics, magnetic and catalysis. Several techniques have been proposed for the deposition of metal nanoparticles containing a-C:H films, including gas evaporation [8], sputter deposition [9,10], plasma-enhanced chemical vapor deposition [11]. However, the applications of composite films have been limited owing to the complicated equipment, rigorous condition of preparation and the by-product such as metal carbides and carbonaceous constituents in these vapor deposited methods.

The electrolysis of organic liquids has been demonstrated great promising to fabricate a-C:H films recently [12–14]. The liquid-phase electrodepositing techniques have many advantages such as availability for large area deposition on irregular shape substrates, low deposition temperature, and simplicity of the setup. Jiang et al. [15] and Huang et al. [16] have reported that copper-doped diamond-like

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carbon films could be obtained using an electrochemical method by choosing the copper salt solution as electrolyte. However, the carbon source is a covalent compound but the metal dopant is ionic compound, so the metal is more easily deposited than carbon under the same electrolysis conditions, which makes it difficult to control the co-deposition of carbon and copper. However, zero-valence metal nanoparticles, which are chemically stable in the deposition process, would not participate in the electrochemical reaction, therefore, it is reasonable to achieve the co-deposition of carbon and metal using metallic nanoparticles instead of metal salt as dopants.

In this communication, we report a novel electrochemical route for the preparation of Au nanoparticles (Au NPs) incorporated in a-C:H films on single crystal silicon substrates where nanosized Au particles are suspended in the electrolyte and co-deposited with the carbon. This method could homogeneously disperse nanoparticles in the a-C:H matrix, which significantly simplify the preparation process and make it more cost-effectively. Then, the related reaction mechanism of the deposition is also discussed and the electrical properties of the composite films are evaluated.

2. Experimental

A simple electrolytic cell system similar to that of depositing pure DLC films [13] was used to prepare the Au-a-C:H composite films. A clean Si (1 0 0) substrate with a size of $10 \times 20 \times 0.3\ \mathrm{mm}^3$ and a polished graphite plate were used as negative and positive electrodes, respectively. The distance between the two electrodes was set to 7 mm, and the films were deposited under an applied potential of 1200 V and at a bath temperature of 50 °C. Methanol was chosen as carbon source and the Au nanoparticles with a mean diameter of 50 nm synthesized following the literature [17] as dopant. In order to ensure that the nanoparticles are uniformly dispersed, the electrolyte was subject to ultrasonic vibration and magnetic stirring for 30 min before electrolysis process. Here, the concentration of the Au nanoparticles in the electrolyte was 0.1 mM and the content of Au in the film could be controlled simply by changing the Au concentration in the electrolyte. During the deposition, the electrolyte was magnetically stirred to promote the diffusion of solution. The electrolysis current density was monitored in the range of $10–15\ \mathrm{mA\ cm}^{-2}$, similar to that when only the pure methanol was used as electrolyte, which might be attributed to that elementary Au nanoparticles did not participate in the electrochemical reaction. The deposition time was set to 5 h to obtain an ivory-white translucent film.

The surface morphology of the films was observed with an SPM-9500 atomic force microscope (AFM). Renishaw Raman spectroscopic measurements were carried out to investigate the structure of the surface of carbon films, using an Ar^+ laser of 514.5 nm and a resolution of $1\ \mathrm{cm}^{-1}$. X-ray photoelectroscopic (XPS) measurements were performed on a Perkin-Elmer PHI-5702 system equipped with a hemispherical analyzer, to investigate the chemical composition of films. FTIR spectra of the composite films were recorded on a Bio-Rad FTS165 spectrometer at a resolution of $4\ \mathrm{cm}^{-1}$ with air as the background. The morphology and size of the Au nanoparticles were determined based on a JEM-1200EX transmission electron microscope (TEM) observation at an accelerating voltage of 100 kV. The sheet resistivity of the films was measured using the four-point probe station.

3. Results and discussion

The surface morphology of Au nanoparticles incorporated a-C:H film was studied by atomic force microscopy (AFM). The typical AFM (3D) image (not shown) indicates that the composite carbon film, composed of small and compact spheres, is uniform and smooth. The chemical composition of composite film was analyzed by X-ray photoelectron spectroscopy (XPS) so as to distinguish if the dispersed Au nanoparticles reacted with carbon or just were hidden in carbon film. The XPS survey spectrum of the film indicates that the film consists mainly of carbon, aurum and oxygen. The observed O 1s peak is common for the spectra of this kind of film, which might be designated to the contamination of the sample exposed to air. As depicted in Fig. 1a, the C 1s binding energy of the composite film is about 285.1 eV, which is in good agreement with that of the as-deposited pure a-C:H film. The peaks

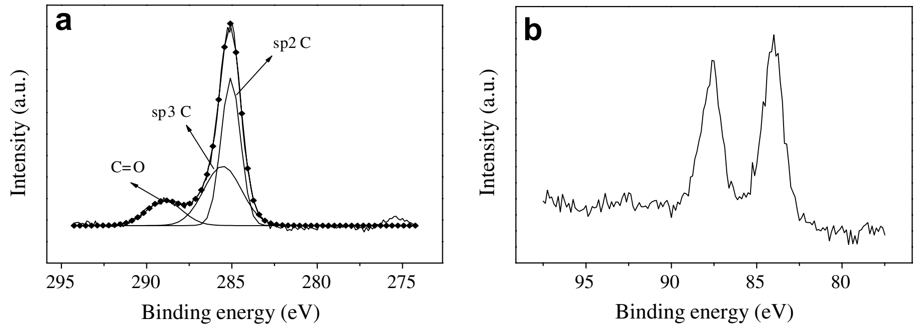

Fig. 1. XPS spectra of Au NPs contained a-C:H film: (a) deconvoluted C1s; (b) Au4f.