Fabrication of ZnO nanoparticles-embedded hydrogenated diamond-like carbon films by electrochemical deposition technique

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ZnO nanoparticles-embedded hydrogenated diamond-like carbon (ZnO-DLC) films have been prepared by electrochemical deposition in ambient conditions. The morphology, composition, and microstructure of the films have been investigated. The results show that the resultant films are hydrogenated diamond-like carbon films embedded with ZnO nanoparticles in wurtzite structure, and the content and size of the ZnO nanoparticles increase with increasing deposition voltage, which are confirmed by X-ray photoelectron spectroscopy (XPS), Raman, and transmission electron microscope (TEM). Furthermore, a possible mechanism used to describe the growth process of ZnO-DLC films by electrochemical deposition is also discussed.

Keywords: diamond-like carbon, ZnO nanoparticles, electrochemical deposition, microstructure

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1. Introduction

Zinc oxide (ZnO) is a self-activated II–VI semiconductor with hexagonal wurtzite structure and a band gap of 3.37 eV at room temperature. As an important semiconductive and piezoelectric material with several applications in optoelectronics and sensors, ZnO has been paid considerable attention since 1997.[1–3] However, bulk ZnO is a relatively soft material possessing a Young's modulus value of about 140 GPa in [0001] direction, and this induces the problem of not being able to fully utilize ZnO in device fabrication, for which good mechanical properties are generally desired. Moreover, owing to the growing demand for miniaturization of optoelectronic devices, ZnO nanostructures draw more and more interest, but in practice the ZnO nanomaterials should be able to withstand harsh environments. Hence, there is a strong requirement of studying the feasibility of embedding ZnO nanomaterials within hard protective materials.

Diamond-like carbon (DLC) consists of a mixture of sp^2 and sp^3 bonded carbon and a low percentage of hydrogen, showing many properties similar to that of diamond, including high hardness, low friction coefficient, negative electron affinity, high thermal conductivity, and chemical inertness. The DLC possesses a Young's modulus value of around 700 GPa due to the strong sp^3 bonding, and has widespread applications as prospective coatings in many fields such as optical windows, magnetic storage disks, car parts, microelectromechanical systems, and biomedical applications like artificial hearts.[4–7] By embedding ZnO nanoparticles into DLC films, which can act as a hardshell or protective casing, the mechanical properties of ZnO can be complemented effectively. Furthermore, the optoelectronic properties of the films can be tuned by adjusting the ZnO particle size, which may further broaden the application areas of DLC films in optoelectronics. Hsieh *et al.*[8] first reported the embedding of ZnO into DLC film by high vacuum filtered cathodic vacuum arc (FCVA) technique, and detected strong monochromatic emission from the composite film.

The liquid electrochemical deposition of DLC films, first performed by Namba[9] in 1992, has drawn much interest, for the advantages over chemical vapor deposition (CVD) and physical vapor deposition (PVD), including less consumption of energy, simple technical devices, low temperature, and other advantages common to the galvanic deposition process.[10–12] It has been reported that the incorporation of a few atomic percentages of metal or metal oxide, such as Fe, Au, and TiO_2, into DLC films by electrochemical deposition is possible, and generally forms carbon nanocomposite mixtures.[13–15]

In this paper, we attempt to prepare the ZnO nanoparticles-embedded DLC (ZnO-DLC) films, making use of the electrolysis of methanol-$Zn_2[C_{32}H_{42}N_8O_{13}]Cl_{44}$ solution. This new strategy could provide a novel deposition method for DLC nanocomposites, with the aid of electrochemical deposition. Based on the analysis results, a possible mechanism used to describe the growth process of ZnO-DLC films by electrochemical deposition is discussed. Moreover, the ZnO nanoparticles embedded in a carbon matrix may have potential applications in optoelectronic devices.

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2. Experimental setup

The ZnO-DLC films were prepared in an electrolytic cell system, similar to that reported in Ref. [9]. An n-type (100) silicon substrate (10 mm×20 mm×1 mm) with a sheet resistance of ∼7–13 Ω/cm^2 was mounted on the negative electrode. A platinum foil with a bare smooth surface was used as the anode and kept at 7 mm away from the negative electrode. Just before deposition, the Si substrates were firstly immersed in 5% HF solution to remove the native oxide layer, subsequently ultrasonically cleaned in deionized water, ethanol, and acetone, respectively, and then dried by nitrogen gas blowing immediately. An organic compound $Zn_2[C_{32}H_{42}N_8O_{13}]Cl_{44}$ was synthesized to serve as the Zn source in the electrochemical deposition. For ZnO incorporation, the electrolytic solution was prepared by dissolving $Zn_2[C_{32}H_{42}N_8O_{13}]Cl_4$ in analytically pure methanol, with the concentration of 0.08 g/ml. Two different voltages of 800 V and 1200 V were chosen and kept constant in the deposition process. The temperature was controlled at 50–60 °C. The deposition process lasted for 8 h.

The composition of the films was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-5702). The surface morphologies of the films were observed by atomic force microscopy (AFM, CSPM4000). The microstructure was investigated by a micro-Raman system (Jobin-Ivon LabRam HR800) with a laser source at wavelength of 532 nm, transmission electron microscopy (TEM, JEM-1200EX), and selected area electron diffraction (SAED).

3. Results and discussion

After deposition, gray films were obtained on the Si substrates. XPS measurements were performed to investigate the chemical composition and bonding state of the composite films. For the ZnO-DLC films deposited under 800 V and 1200 V, the ratios of Zn/(Zn+C), calculated from the survey spectra, are 9.52 at% and 11.5 at%, respectively, indicating that the Zn element has been successfully incorporated into the carbon matrix and the content increases with increasing deposition voltage. Figures 1 and 2 show the bonding energy of Zn_{2p} and C_{1s}, respectively. It is seen that the Zn_{2p} photoelectron spectra exhibit two main peaks around 1045.4 and 1022.4 eV, which are assigned to $Zn_{2p^{1/2}}$ and $Zn_{2p^{3/2}}$, respectively. The Zn_{2p} spectra are consistent with those of ZnO nanoparticles,[16] which reveals that the Zn atoms are bonded to O atoms to form ZnO instead of Zn–C–O alloys. With deposition voltage increasing, the two Zn_{2p} peaks both downshift slightly for the possible reason that the size of ZnO nanoparticles in the DLC matrix increases with increasing Zn content, resulting in the reduction of surface atoms with higher binding energy than bulk atoms. The binding energies of the C_{1s} peaks range from 284.5 V to 285.5 eV, as shown in Fig. 2. It is usually assumed that DLC films consist of both sp^3 and sp^2 bonded carbon atoms. Thus, their corresponding C_{1s} peaks may con-

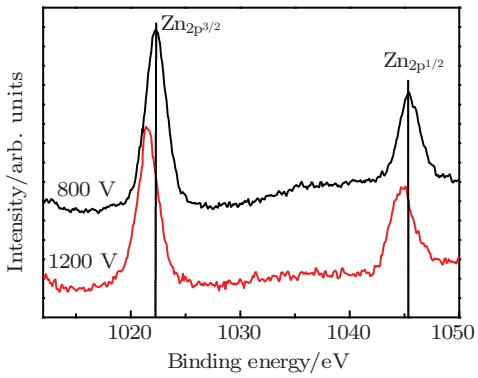


Fig. 1. (color online) The Zn_{2p} XPS spectra of the ZnO-DLC films.

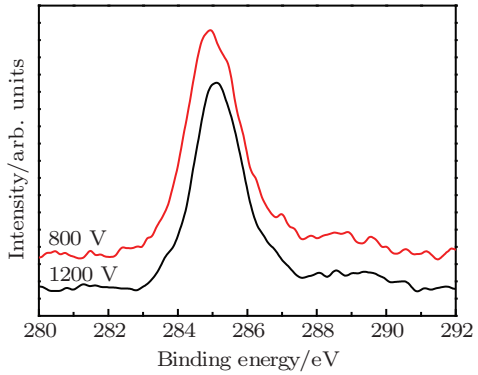


Fig. 2. (color online) The C_{1s} XPS spectra of the ZnO-DLC films.

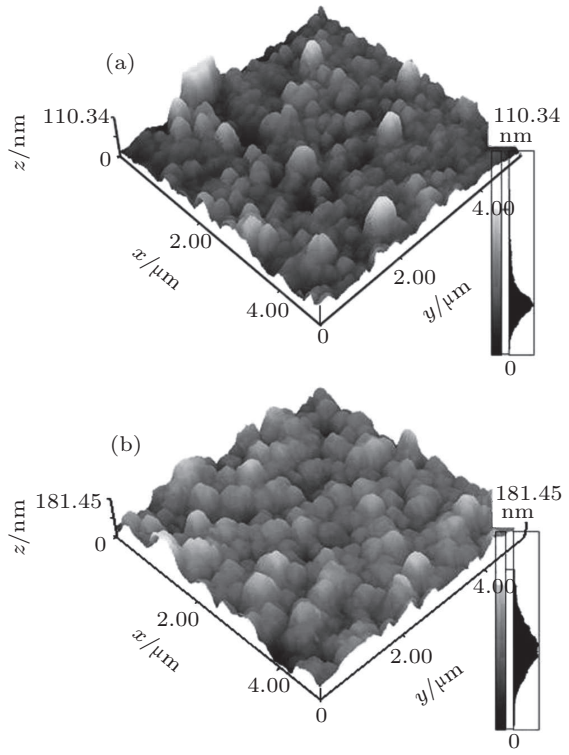


Fig. 3. The 3D AFM surface micrographs of the ZnO-DLC films deposited under (a) 800 V and (b) 1200 V.

sist of two groups of C_{1s} photoelectrons, one of which is at 284.8 eV from the carbon atoms in the sp^2 configuration, and the other one is at 285.3 eV from the carbon atoms in the sp^3 configuration.[17] The C_{1s} peak shifts to higher binding energy with increasing deposition voltage, suggesting that the sp^3/sp^2 ratio in the ZnO-DLC film deposited under 1200 V is higher. Figures 3(a) and 3(b) show the three-dimensional (3D) AFM surface micrographs of the resultant films. The ZnO-DLC film deposited under 1200 V shows a higher roughness than under 800 V. This may result from the inhomogeneity of film forming during the deposition process. When the ZnO molecules were embedded into a DLC amorphous matrix, we obtain ZnO particles, and the surface roughness increases.

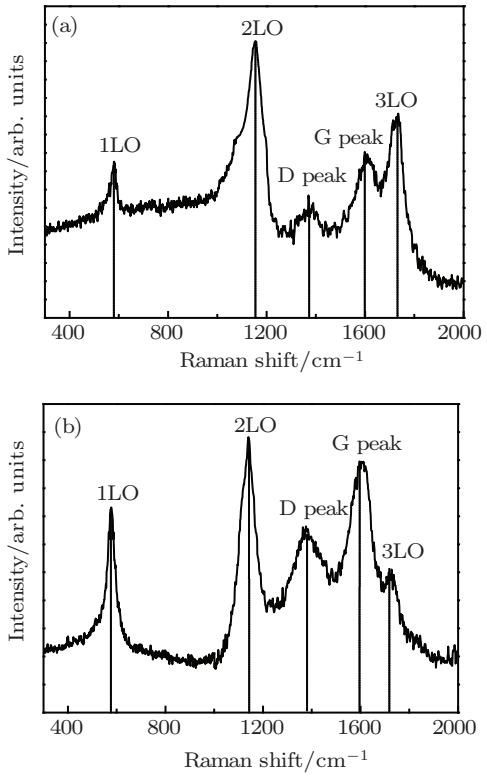


Fig. 4. The Raman spectra of the ZnO-DLC films deposited under (a) 800 V and (b) 1200 V.

In order to have in-depth understanding of the microstructure of the ZnO-DLC films, Raman measurements have been carried out. Figures 4(a) and 4(b) show the Raman spectra of the ZnO-DLC films electrochemically deposited under 800 V and 1200 V, respectively. For both the composite films, D and G peaks appear in the range of 1200–2000 cm^{-1}, which is consistent with obvious DLC characteristics of the carbon matrix.[4] It is seen that both the D and G peaks shift to lower wavenumbers with increasing deposition voltage. According to the theory of Robertson, this result indicates the increase in the sp^3/sp^2 ratio in the DLC matrix,[4] which is in accordance with the XPS analysis, can be interpreted by the experimental result of Yan *et al.*, where the increase in electrochemical deposition voltage will induce an increase in sp^3 content in the resultant DLC films.[11] In addition to D and G peaks, a number of LO multi-phonon peaks corresponding to ZnO nanoparticles are observed in the Raman spectra of the ZnO-DLC films. The peak at 577 cm^{-1} is related to longitudinal optical (LO) phonon mode of ZnO nanoparticles.[18] A 4-cm^{-1} redshift of the 1LO peak has been observed for the deposited ZnO-DLC film at 800 V, which may be caused by the spatial confinement within the particle boundaries. In the high-frequency region, LO overtones and combinations involving LO modes induce a second-order feature peak near 1140 cm^{-1}.[19] However, the strength of observed peaks is too intensive to be caused by the LO peak of ZnO only. Possible explanation should take the ν_1 mode of trans-polyacetylene (trans-PA) in the DLC matrix into account.[20]

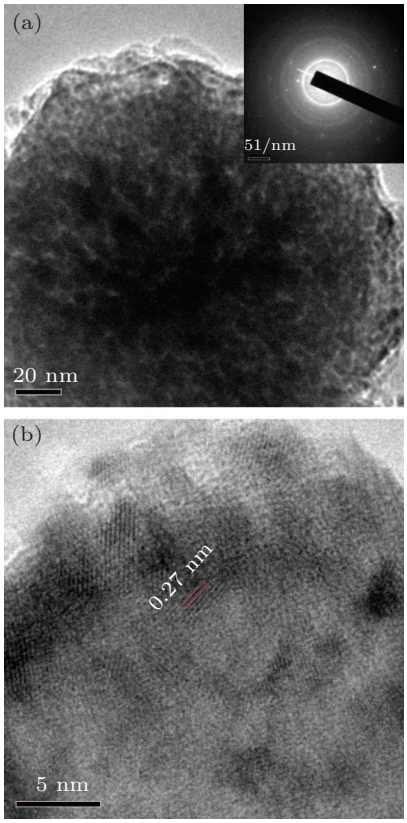


Fig. 5. (a) TEM image and selected area diffraction (SAED) and (b) HRTEM images of the ZnO-DLC composite film.

TEM and high-resolution TEM (HRTEM) images of ZnO-DLC composite film deposited under 1200 V are shown in Fig. 5. The spherical ZnO nanoparticles (dark spots) with diameter of about 4 nm are uniformly embedded in amorphous carbon matrix (bright area), and show no clusters. The inset SAED pattern composed of dispersed diffraction spots and concentric diffraction rings reveal the nanopolycrystalline structure existing in the film. In the HRTEM image, the lattice spacings between adjacent lattice planes are approximately 0.27 nm, in agreement with the distance between two (002) crystal planes of hexagonal wurtzite structural ZnO,[21] which conforms that the ZnO nanoparticles embedded in DLC

film are in wurtzite structure. It can thus be concluded that ZnO nanoparticles in wurtzite structure have been successfully embedded within DLC films by electrochemical deposition method, and the DLC matrix can availably prevent the ZnO particles from agglomeration.

On the basis of the experimental results, a mechanism is proposed to interpret the growth process of the ZnO-DLC films by electrochemical deposition technique. The electrochemical deposition of DLC films is different from traditional electrochemical technique for the dielectric organic solvents are used as the electrolyte. In the deposition processes, organic molecules undergo polarization, ionization, and decomposition under high voltage applied between two electrodes, resulting in single-carbon species CH_3^+ ions, which will further concentrate near the cathode surface and form DLC films. For metal doping, such as Au, the corresponding metal nanoparticles were generally dispersed in the electrolyte by stirring, and then the particles could be incorporated in the DLC films, but the uniformity of the metal particles in the composite films cannot be ensured in the electrochemical deposition process. In this work, $Zn_2[C_{32}H_{42}N_8O_{13}]Cl_4$ super molecules were chosen to be ZnO precursor, for the reason that the zinc compound could be well dissolved in methanol, and the content and size of ZnO nanoparticles could be adjusted by varying the concentration of $Zn_2[C_{32}H_{42}N_8O_{13}]Cl_4$ in electrolytes. Based on the above discussion, the growth procedure may include the following steps.

1) Under high applied potential, methanol molecules will be polarized and further ionized, producing CH_3^+ species. Super molecules $Zn_2[C_{32}H_{42}N_8O_{13}]Cl_{44}$ will be ionized synchronously to provide Zn precursors and facilitate an electric double layer forming on the cathode surface to further accelerate the methanol ionization as follows:

$$CH_3OH \rightarrow CH_3^+ + OH^-,$$
$$Zn_2[C_{32}H_{42}N_8O_{13}]Cl_4 \rightarrow 2Zn^{2+} + C_{32}H_{42}N_8O_{13} + 4Cl^-,$$
$$C_{32}H_{42}N_8O_{13} \rightarrow C_{32}H_{42}^+ + N_8O_{13}^-.$$

2) Due to the liberation of Joule heat in the electrochemical process, high-temperature grades will appear and gasify the organic electrolyte near the substrate, leading to a micro region with transient non-equilibrium high temperature and pressure near the cathode surface, which is very similar to the reactive conditions in plasma-enhanced CVD.[22,23] Owing to the synergism of the higher electric field and localized high temperature as well as an electron-enriched sheath around the cathodic substrate, the thermochemistry, plasma chemistry, and electrochemistry processes will occur within this region. The above-mentioned process has advantages over the following electrochemical reactions.

3) The Zn^{2+} ions migrate to the cathode surface, and react with methanol molecules, forming ZnO nanoparticles embedded in amorphous carbon matrix, and further forming ZnO-DLC composite films

$$Zn^{2+} + 2e + CH_3OH \rightarrow ZnO,$$
$$nZnO + mCH_3^+ + me \rightarrow ZnO - DLC + H_2\uparrow.$$

The product is the DLC film embedded with ZnO nanoparticles in wurtzite structure, which is confirmed by the above experimental analysis. The actual deposition process is very complex and needs further research.

4. Conclusions

In summary, the ZnO nanoparticles-embedded DLC films were deposited by the electrolysis of the $Zn_2[C_{32}H_{42}N_8O_{13}]Cl_{44}$-methanol solution at low temperature and atmospheric pressure. The ZnO nanoparticles embedded in DLC matrix are in wurtzite structure. The size of the ZnO nanoparticles and the sp^3 content of the DLC matrix both increase with increasing deposition voltage. The electrochemical deposition mechanism of the ZnO-DLC films is discussed, including the synergism of the thermochemistry, plasma chemistry, and electrochemistry process. The electrochemical deposition of ZnO-DLC films may open the potential applications of the system in microelectronic and optoelectronic devices.

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