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LETTER

Direct hydrothermal electrochemical preparation of diamond-like carbon films on substrates

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Introduction

Diamond-like carbon (DLC) films have been the subject of huge scientific and technological efforts due to their interesting physicochemical, mechanical, and electrical properties. And the films present numerous feasible applications in electronics, mechanics, gas storage, biomedical engineering, etc. Recently, it has been reported that DLC film could be prepared using various types of chemical vapor deposition (CVD) [1–5] and electrochemical method [6–8].

In this paper, an inexpensive and environmentally friendly hydrothermal electrochemical process [9–12] was developed for preparing DLC thin films. The results of structural characterization of such films were also reported.

Experimental

Ta substrates with $10 \times 10 \times 0.1$ mm^3 dimensions of 99.9 wt% purity were mechanically polished and degreased with acetone using an ultrasonic cleaner. The reaction solutions were prepared by dissolving 0.19 g (0.001 mol) of glucose into 100 mL of distilled water.

The detailed description of the deposition facility and the growth method has been done elsewhere [9]. Typical preparation conditions are galvanostatic condition with the applied potential of 0–5 V, the current density of 0–0.01 mA/cm^2, working temperature of 180 °C and working time 20 h. After each experiment, the Ta substrates covered with brown yellow films were washed with water, ultrasonically in ethanol, and air-dried prior to characterization.

The morphology observation of films were conducted using scanning electron microscopy (SEM, JSM-6301F) along with energy dispersive spectroscopy (EDS), Raman spectroscopy (Labram HR 800, Jobin–Yvon), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet Nexus670) were employed to characterize their structure parameters.

Results and discussion

SEM and ESD characterization

The typical SEM morphology of the as-deposited DLC films was shown in Fig. 1. The film surface was very smooth. The thickness of the films measured from a Ta sample was about 1.2 μm. The film adhered well to the Ta substrates even after being fractured mechanically.

The EDS survey spectra (Fig. 2) displayed the peaks attributed to carbon and oxygen as well as to the substrate of Ta. EDS could take about more than 1 μm thickness from the surface, so some peaks attributed to the components of the substrate (Ta) were observed in the EDS spectra. Not considering the influence of the Ta substrate, the atomic ratio of C to O in the film was 100:14. While the oxygen content of hydrothermal carbon particle was more than 20% [13]. So the film prepared by hydrothermal electrochemical method consist more carbon than hydrothermal carbon particle.

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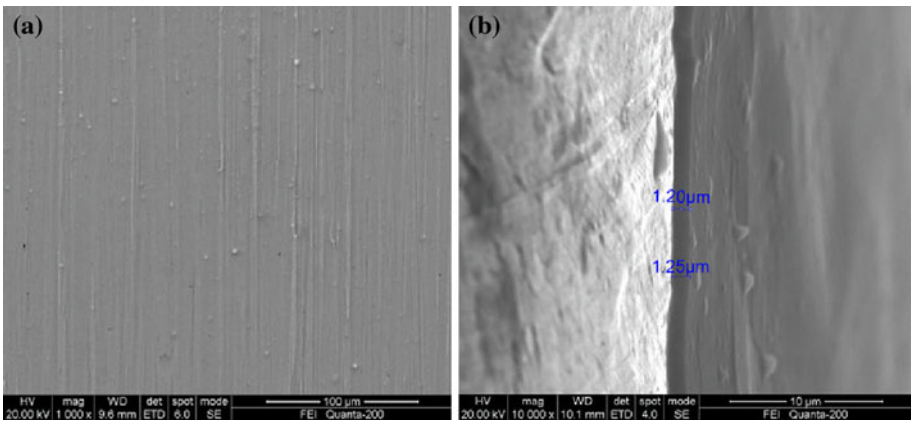

Fig. 1 SEM micrograph of DLC film prepared at 180 °C **a** surface, **b** cross section

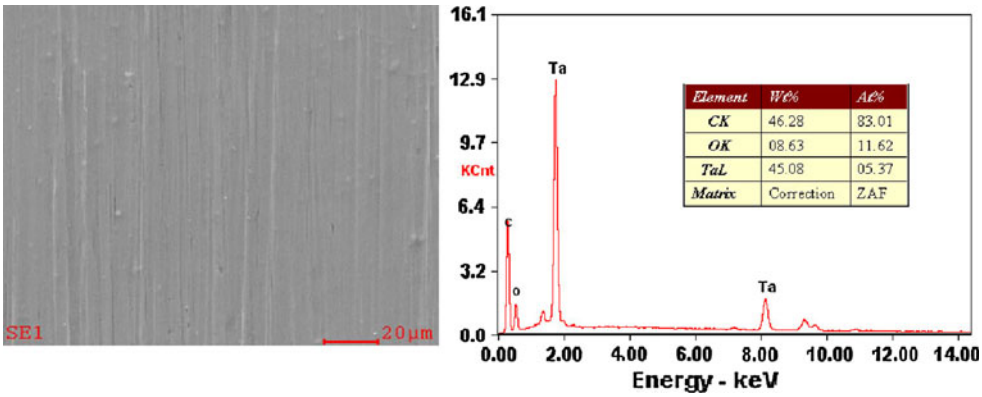

Fig. 2 ESD topography images of DLC films

Bonding characteristic of the films

Raman spectroscopy is considered to be the best way to check the detailed bonding structure of diamond and DLC films. It is a straightforward, non-destructive technique. Raman spectra of the as-deposited film are shown in Fig. 3. All the spectra in this study presented similar characteristics. As shown in Fig. 3, the wave number of the spectra between 1000 and 2000 cm^{-1} could be accurately fitted by three Gaussians of 1130 cm^{-1} band, 1346 cm^{-1}(called the D line) and 1550 cm^{-1} (called the G line) bands. And the full width at half maximum (FWHM) of the three fitted bands were 92, 249, and 124 cm^{-1}, respectively. Shroder et al. [14, 15] suggested that the feature of 1130 cm^{-1} band was due to regions of microcrystalline diamond, amorphous diamond, or disordered *sp*3-bonded carbon which forms as a precursor to diamond formation. The D and G peaks were assigned to disordered carbon and *sp*2 carbon bond, respectively. The intensity ratio of D band to G band (I_D/I_G) was 1.27. These indicate that there are typical diamond and amorphous carbon with a mixture structure of *sp*2 and *sp*3 carbon phases in the prepared film.

To further investigate the structure of the films in detail, we used attenuated total reflectance Fourier transform infrared spectroscopy to characterize the films. Figure 4 depicts the ATR-FTIR spectrum acquired from the

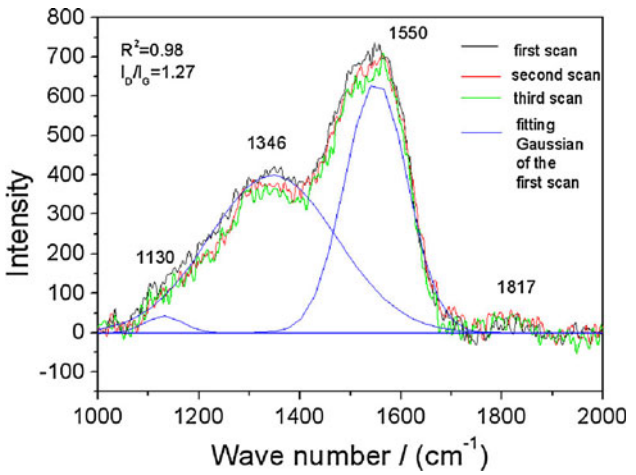

Fig. 3 Raman spectra of carbon film

prepared film. The ATR-FTIR spectrum for films indicates four main features centered around 943.0, 1102.5, 1598.9, and 3237.8 cm^{-1} could be observed. The two peaks centered at 1102.5 and 3237.8 cm^{-1} may be attributed to the vibrational modes for O–H band [16]. It implies the existence of a large number of residual hydroxyl groups. The O–H broad band was also observed in the carbon films prepared by electrolysis of organic solutions [8, 17, 18]. The peak at around 1598.9 cm^{-1} is a characteristic to *sp*2

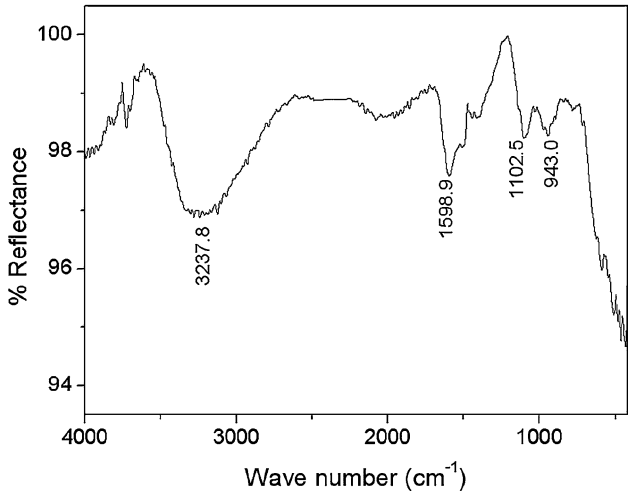

Fig. 4 FTIR spectrum of the carbon film

C=C for the as-deposited DLC films [19]. In Fig. 4, the small peaks at 1500 and 700 cm^{-1} can be the characteristic bands attributed to C–C vibrational modes of aromatic compounds. The peaks could be observed in hydrothermal carbon [20, 21], and the intensity was strong. No C=O bond centered around 1714 cm^{-1} [21] was observed. To summarize, the spectroscopic data indicate that a significant number of *sp*2 C=C functional groups are present on the film.

Conclusion

Diamond-like carbon (DLC) thin films were prepared by the hydrothermal electrochemical technique using glucose as carbon source in this study. The DLC film presented carbon and oxygen, and their atomic ratio was 100:14. The film had D and G typical DLC Raman peaks and C=C ATR-FTIR peak.

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