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Fabrication of hydrophobic fluorinated amorphous carbon thin films by an electrochemical route

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Abstract

A novel electrochemical route for the preparation of hydrophobic fluorinated amorphous carbon (a-C:F) films with nanostructured surfaces on single crystal silicon substrate was reported. The films were investigated in terms of the surface morphology, chemical composition, microstructure and hydrophobic behavior. The results showed that a highly uniform and densely packed bamboo shoot-like nanostructure was obtained without any use of template. The incorporation of fluorine presented mainly in the forms of CF_2 chains and $C{=}CF_x$ ($x = 1, 2$) in the films. Sessile drop water contact angle measurements showed that the contact angle of a-C:F films deposited by electrochemical route was about 145°, which can be attributed to the lower surface energy of CF_x groups and higher diffusion resistance of the special nanostructured surface to water. Moreover, the related growth mechanism of the resulting films in liquid-phase electrodeposition is discussed as well.

Keywords: Fluorinated amorphous carbon; Electrochemical deposition; AFM; FTIR; Hydrophobic effect

1. Introduction

Recently increased interest has been focused on the effect of fluorine addition to diamond-like carbon (DLC) films. It has been reported that a-C:F films have been considered as the most promising candidates for intermetal dielectric materials applied in the next generation ultra-large scale integration devices for their low dielectric constant, chemical inertness, low moisture absorption, high thermal stability, high mechanical strength, and good adhesion to the neighboring layers [1,2]. On the other hand, the incorporation of fluorine into DLC films will greatly reduce its surface free energy but almost keep DLC-behavior [3,4]. Bestowing hydrophobicity to DLC films with superior mechanical properties makes it possible to be used in many applications such as moisture resistant lubricants, lithium battery cathode, or protective coatings for optics.

Generally, there are two ways to modify DLC with fluorine, i.e., plasma surface processing [5] and deposition treatment by a variety of different techniques [6,7]. However, these methods are all vapor deposition techniques. The applications of the resulting films have been limited owing to the complicated equipment and rigorous preparation conditions in the vapor deposition.

A liquid-phase electrochemical technique to deposit amorphous carbon films making use of electrolysis of organic liquids might be more attractive [8,9], which is with the advantages of availability for large area deposition, low deposition temperature, low cost, and simplicity of the setup, over the above-mentioned vapor deposition techniques. Many previous experiments have proved that most of materials deposited from vapor phase can also be deposited in liquid phase using electrodepositing techniques [10]. So it is reasonable to obtain a-C:F films, although the

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deposition of a-C:F films by an electrochemical route has not been reported up to now.

In this letter, an electrochemical route to deposit a-C:F films from the methanol solution of 2,2,2-trifluoroethanol (CF_3CH_2OH, TEF) at atmospheric pressure and low temperature was presented. The choice of such fluoride dopant is based on the assumption that the similar structural formula and property between the dopant and the carbon source might be beneficial to the linkage of fluorine atoms to the amorphous carbon matrix. The addition of fluorine to the amorphous carbon matrix greatly increased the hydrophobicity, with contact angle (CA) of water about 145°. The hydrophobicity of the resulting films is evidently more excellent than that of the a-C:F films prepared by the vapor deposition technique ($CA < 110°$) and analogous hydrophobicity of doped amorphous carbon films has never been reported before. It is believable that the results reported here may have potential applications in microelectronic devices and optical apparatus.

2. Experimental

A simple electrolytic cell system similar to that reported in Ref. [8] was used to prepare the a-C:F films. The silicon (100) substrate with a sheet resistance about 5–20 Ω/cm^2 was mounted on the negative electrode. A graphite plate was used as the counter electrode, 7 mm away from the negative electrode. 2,2,2-Trifluoroethanol (TEF purity 99.8%, ACROS) was dissolved in analytically pure methanol (purity $\geqslant$99.5%) with volume ratio of TEF to methanol 1:9. The cleaned substrate with an area of $1.0 \times 2.0\ cm^2$ was placed into the above solution to conduct the deposition of the composite films at a temperature of 50 °C, a DC power-supply voltage of 1200 V, for 5 h. During the deposition, the electrolyte was magnetically stirred to promote the diffusion of solution. As compared, the pure carbon films were deposited by the electrolysis of methanol at the same conditions.

The surface morphology of the films was observed with an SPM-9500 atomic force microscope (AFM). Renishaw Raman spectroscopic measurements, with an Ar^+ laser of 514.5 nm and a resolution of $1\ cm^{-1}$, were carried out to investigate the structure of carbon films. X-ray photoelectron spectrum (XPS) measurements were performed on a Perkin–Elmer PHI-5702 system equipped with a hemispherical analyzer to investigate the chemical composition of the films. Fourier transformation infrared spectrometry (FTIR) spectra of the composite films were recorded on a Bio-Rad FTS165 spectrometer at a resolution of $4\ cm^{-1}$ with air as the background. The sessile drop method was used for water contact angle measurements with a contact angle goniometer (Modle 100-00, Ramé-hart Inc., Mountain Lakes, NJ, USA).

3. Results and discussion

After the deposition, ivory-white translucent films were obtained on the cathode Si substrates by the electrochemical route. Fig. 1a shows the typical two-dimensional AFM surface image of fluorinated carbon films prepared by the electrodeposition method. It is seen that the films are composed of uniform and well-defined nanospheres of about 100 nm in mean diameter but the nanospheres on the top surface accumulate uncompactly. Because of the limited contrast in the two-dimensional AFM image, the presence of nanoporous structure is revealed unambiguously only in the topographical image of Fig. 1b. It shows that a highly uniform and densely packed bamboo shoot-like nanostructure was obtained without any template used. Moreover, the silicon substrate with an atomic smooth surface has little effect on the surface morphology of the films.

The Raman spectrum (not shown) from the as-deposited sample resembles the typical Raman spectra obtained from the pure amorphous carbon films deposited under the same experimental conditions, which suggests that the as-deposited film is a kind of amorphous carbon with diamond-like structure. The chemical compositions and bonding states of the films were analyzed by XPS. From the integrated area of C 1s and F 1s peaks divided by their sensitivity (0.78 for C 1s and 1.00 for F1s, respectively), the fluorine to carbon ratio in the films was calculated to be about 0.21 which was more lower than that in PTFE. To get detailed chemical bonding state, the fittings of the C1s and F1s core level peak were performed by approximating the contribution of the background by the Gaussian method, showed in Fig. 2. As observed, the C1s peak is obviously broadened at high energy with the incorporation of F into the films due to the fact that electro-negativity of F is greater than that of C. The C1s core level spectra can be curve-fitted with peak components having binding energies at 285.0 eV for the C–(C, H) species, at 286.6 eV for the C–CF_x ($x = 1$–3) species, at 288.0 eV for the CF species, at 289.6 eV for the CF_2 species [11–13]. The F1s core level spectra can be well decomposed into two peak components associated with CF (686.5 eV) and CF_2 (687.4 eV) species, respectively. XPS result suggests that fluorine atoms bonded with carbon atoms of the film to form CF_2 and CF bonds.

FTIR is a very powerful instrument to detect the chemical structure of the a-C:F films. Fig. 3 provides the IR absorption spectra between 625 and $2000\ cm^{-1}$ of the sample. The strong IR absorption in this region originates from carbon–fluorine and carbon–carbon vibration modes. It is found that the spectra consist of two broad bands: one in the region of 1000–$1400\ cm^{-1}$ corresponding to CF_x ($x = 1$–3) groups vibration modes, the other in 1400–$1900\ cm^{-1}$ corresponding to C=C vibration modes [11,14–16]. The broad absorption band in the range of 1000–$1400\ cm^{-1}$ arises from the overlapping absorbance of many CF_x species ($x = 1$–3) in which the shoulder peak located at $1220\ cm^{-1}$ is assigned to CF_2 stretching vibration. [14,15] The C=C ring stretch at $1502\ cm^{-1}$ and the hydrogenated, fluorinated C=C stretch at $1600\ cm^{-1}$ are the two significant absorption bands in