Synthesis of silicon carbide nitride nanocomposite films by a simple electrochemical method

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Abstract

Silicon carbide nitride (SiCN) nanocomposite films have been deposited on silicon substrates by using of a simple electrochemical method from a methanol solution of hexamethyldisilazane ((CH 3)3-Si-NH-Si-(CH3)3, HMDSN) at atmospheric pressure and low temperature. The electrodeposited composite films were characterized by XPS, FTIR, XRD, and AFM, respectively. As the results, the films are amorphous carbon films containing β-Si3N4, α-Si3N4, and SiC crystalline grains. The introduction of HMDSN contributes to promote the growth of the carbon films and leads to the formation of the Si3N4 and SiC crystalline grains.
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1. Introduction

The synthesis of silicon nitride and silicon carbide has been widely studied due to their attractive properties, such as wear resistance, chemically inertness, and wide band gap, which have already provided optical, electronic and other applications in aggressive ambient. Recently, SiCN alloys have also motivated much attention because they might have intermediate properties or performances even better than those of the two barriers.

Therefore, the synthesizing process of SiCN compounds is growing rapidly. So far, many chemical and physical vapor deposition techniques have been claimed to prepare amorphous or crystalline silicon carbon nitride films, i.e., microwave plasma chemical vapor deposition [1], magnetron sputtering [2], ion or plasma sputtering [3], ion implantation [4], and so on. However, their applications have been limited owing to the complicated and costly equipment and rigorous preparation conditions, such as high substrate temperature and high vacuum.

The possibility of deposition of diamond-like carbon (DLC) films by means of electrolysis of organic liquids such as methanol [5], acetonitrile [6], dimethylsulfoxide [7], and lithium acetylide in dimethylsulfoxide [8,9], at atmospheric pressure and low temperature, has been demonstrated recently. From the application viewpoint, the liquid deposition techniques have many advantages such as availability for large area deposition on intricate surfaces, low deposition temperature, low consumption of energy, and simplicity of the set up, over the vapor deposition techniques. Recently, we have successfully prepared DLC/nanosilica composite films by an electrochemical route [10]. This novel method provided a new deposition strategy for DLC nanocomposites films by introduction right organic reagent obtaining doping atoms in methanol liquid.

In this communication, an electrochemical route to deposit polycrystalline SiCN nanocomposite films from a methanol solution of hexamethyldisilazane ((CH 3)3-Si-NH-Si-(CH3)3, HMDSN) at atmospheric pressure and low temperature has been reported.
2. Experimental

A simple electrolytic cell system similar to that reported in Ref. [5] was used to prepare the SiCN films. The silicon (100) substrate with a sheet resistance about 7–13 Ω/cm² was mounted on the negative electrode. A graphite plate was used as the counter electrode and kept 6 mm away from the negative electrode. HMDSN was dissolved in analytically pure methanol, with the volume ratio of HMDSN to methanol to be 1:9. The cleaned substrate was placed into the above solution, with an area of 1.0 × 1.5 cm² to be immersed therein, to allow the deposition of the composite films at a temperature of (50 ± 2) °C, a DC power-supply voltage of 400 V, and for deposition duration of 5 h.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin–Elmer PHI-5702 system equipped with a hemispherical analyzer, to investigate the chemical composition of the films. The FTIR of the films were recorded on a Bruker IFS66V Fourier-transform infrared spectrometer, using transmission mode and the freshly cleaned single-crystal silicon wafer as the reference. The crystalline features the sample films were determined on an X’ Pert Philips diffractometer with thin film accessory (using a parallel plate collimator and the diffract angle was only 0.27°), using Ni-filtered Cu Kα (λ = 1.5406 Å) radiation operating at 40 kV and 40 mA. The surface morphology was observed with an SPM-9500 atomic force microscope (AFM) with a Si₃N₄ probe, using “constant force” mode to obtain the morphology image.

3. Results and discussion

During the deposition for the nanocomposite film, we found that the current density decreased slightly from 40 mA/cm² to less than 18 mA/cm² with increasing the deposition time. After deposition a gray film was obtained on the cathode Si substrate. The thickness was measured to be about 600 nm using a surface profiler. The chemical composition of the film was investigated by XPS, and the spectra (shown in Fig. 1) displayed the characteristic peaks attributed to silicon, carbon, nitrogen, and oxygen. The Si2p peak clearly can be split into two peaks, in which the first at 101.5 eV is characteristic of the Si–N bonding while the second at 100.7 eV is attributed to Si–C bonding [11]. The C1s peak can be split two peaks at 284.8 eV and 283.9 eV, which corresponds to the C–C bonding and C–Si bonding, respectively. The N1s peaks at 397.7 eV is in agreement with Si–N bonding [11] and the O1s peak at 532.2 eV is attributed to the adsorbed oxygen on the film surface [12]. It indicates that there are Si–C, Si–N, and C–C bands existing in the electrodeposited film. If esti-
mated in terms of peak area and atomic sensitivity factors, the ratio of Si, N, C, and O in the films expressed by the atomic number ratios, C:Si:N:O, is about 1:0.58:0.41:0.12.

As is known, the FTIR spectrum serves as an indication of the bond vibration in thin films. Fig. 2 gives the FTIR spectrum of a typical sample film. In order to observe more clearly, we magnified the range of 1350–400 cm$^{-1}$ and the full spectrum (4000–400 cm$^{-1}$) was inserted in it. We can see that several Si–C stretching modes are observed, corresponding to wave numbers 610, 650–677, 730–800, 818, and 877 cm$^{-1}$, which are similar to the values reported by other authors for the SiC films [13]. Here we also see a clear Si–N stretching mode at 1104 cm$^{-1}$ due to silicon nitride complex [13,14]. Moreover, absorption peaks appeared at around 434–567 cm$^{-1}$ are observed as well, which are due to the $\beta$Si$_3$N$_4$ crystalline structure [15]. Xiao et al. [11] found that the absorption band at 443 cm$^{-1}$ is attributed to asymmetric stretching of Si–N bond.

The XRD pattern of the sample film is shown in Fig. 3. The spectrum shows various sharp diffraction peaks, which indicate the existence of crystalline structure in the film. The corresponding $d$ of measured film, $\beta$Si$_3$N$_4$ and SiC is given in Table 1, respectively. Since the XRD data of most of the diffraction peaks match that of the theoretically predicted $\beta$-C$_3$N$_4$, $\alpha$-Si$_3$N$_4$ and SiC, it can be concluded that the sample film deposited by the electrochemical technique in the present work contain three polycrystalline phases: $\beta$-Si$_3$N$_4$, $\alpha$-Si$_3$N$_4$, and SiC. No peak is attributed to carbon phase in the XRD patterns of the composite films, which imply that the carbon matrix may be mainly composed of amorphous carbon phases. AFM (3D) picture of the surface morphology of the SiCN film (seen in Fig. 4) shows that the surface is uniform and compact, and is composed of small grains.

In our former paper [16], we have discussed that CH$_3$ species played a critical role in the electrolysis process for the growth of diamond-like carbon films from methanol liquid, which was formed by breaking the covalent bond between the CH$_3$ and OH groups of the methanol at a high enough voltage. These active CH$_3$ species have a higher concentration near the negative electrode surface and pre-
fer the formation of diamond-like carbon film by electrochemical reactions.

The molecule of HMDSN also contains electron-donating methyl group, which displays somewhat positive charge due to their low electro-negativity. Consequently, the molecules are liable to be absorbed on the surface of the negative electrode owing to the sorption of the electrons on the cathode surface. In the electrolysis process, when the supplied energy reaches a certain value, the Si–C and Si–N bonds in HMDSN molecule will be dissociated to form some silicon-containing clusters like \((\text{SiC})_x\) and \((\text{SiN})_x\). The clusters are deposited on the cathode substrate, and form \(\beta\)-Si\(_3\)N\(_4\), \(\alpha\)-Si\(_3\)N\(_4\), and SiC nanoparticles finally.

In the electrodeposited SiCN film, the content of carbon atom is the most (by XPS analysis). Therefore, we think that, in the electrolysis process, the amorphous carbon film is deposited on Si substrate and \(\beta\)-Si\(_3\)N\(_4\), \(\alpha\)-Si\(_3\)N\(_4\), and SiC nanoparticles are wrapped in this carbon matrix. At the same time, we found that, at the same deposition voltage (400 V), there is no carbon film being deposited on Si substrate by electrolysing pure methanol liquid. It is important to note that the HMDSN molecule contains six equivalent methyl groups, thus they would provide a more beneficial microenvironement for the formation of active CH\(_3\) species, and would advance the growth of carbon network and formation of amorphous carbon phase. Consequently, the amorphous carbon matrix and \(\beta\)-Si\(_3\)N\(_4\), \(\alpha\)-Si\(_3\)N\(_4\), and SiC crystals can be deposited on the Si substrate.

4. Conclusion

In summary, the first example of deposition of SiCN nanocomposite films by a simple liquid-phase electrochemical route has been reported. The results of XPS, FTIR, and XRD show that the addition of HMDSN in methanol promotes the growth of amorphous carbon phase and leaded to formation of \(\beta\)-Si\(_3\)N\(_4\), \(\alpha\)-Si\(_3\)N\(_4\), and SiC crystalline grains. This synthesis strategy may be transferred to fabricating other inorganic nanocomposite films, except diamond-like carbon and SiCN films, using appropriate organic reagent and electrolysis condition.

Acknowledgments

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References