Nucleation and growth of amorphous carbon film on tungsten-implanted stainless steel substrates

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Abstract

Amorphous carbon (a-C) films were deposited on W-implanted (20 kV, 3 × 10¹⁷ ions cm⁻²) and un-implanted steel substrates by plasma immersion ion implantation and deposition (PIII&D). The W implantation pretreatment changes the surface structure and impacts film nucleation. Consequently, the growth mechanism of the a-C film is altered resulting in different surface morphologies and roughnesses even though the films deposited on the un-implanted steel substrates possess similar a-C structures as revealed by Raman spectroscopy. The structural differences are probed by X-ray photoelectron spectroscopy and X-ray diffraction. Moreover, microstructural observations were carried out by transmission electron microscopy. A model based on the statistical formation theory is proposed to explain the growth of the a-C films on the implanted and un-implanted substrates.

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1. Introduction

Amorphous carbon (a-C) films have found applications in many areas such as microelectronic and optical devices, biomedical products, corrosion resistant materials, protective overcoats, as well as microelectro-mechanical systems (MEMS) [1–5]. Their unique properties can be attributed to not only the special and interesting properties of the microstructures, but also their surface morphology. The direct use of a-C films on certain materials such as ferrous substrates still faces some technological difficulties. Iron, the main element in stainless steel, enhances the deposition of disordered graphite and carbon has a high rate of diffusion in ferrous substrates, thereby hampering the growth of a-C films. To our knowledge, there have been few reports investigating the a-C growth characteristics on pre-implanted steel substrates.

In this work, a-C films are deposited on 321 stainless steels that have been pre-implanted with W. Ion implantation alters the surface chemistry of the steel substrate and the subsequent growth of the a-C film. The surface morphology and roughness of the a-C film are also affected. The nucleation and growth mechanisms of the a-C films deposited on the pre-implanted and un-implanted substrates are investigated and compared.

2. Experimental details

Coupons of 321 stainless steels (composition in wt. %: Fe: 70.1, C: 0.11, Si: 0.90, Cr: 18.2, Ni: 9.40, Ti: 0.64, S: 0.06 and P: 0.03) were cut into dimensions of 15 × 15 × 2 mm³. The samples were austenitized at 1500 K for 1 h to achieve a solid solution state. They were then polished and cleaned with acetone before treatments.
Tungsten ion implantation was carried out in a multipurpose plasma immersion ion implanter (PIII) equipped with several plasma generating tools including RF discharge, hot filament discharge and vacuum arc metal plasma sources [6–8]. The base pressure in the vacuum chamber was 3 × 10^{-3} Pa. Tungsten PIII was conducted using the following conditions: target bias $V_i = 20$ kV, main arc average current $I_a = 1.0$ A, pulse repetition rate $f = 40$ Hz. Samples 1 and 2 underwent W PIII for about an hour to achieve an approximate implant fluence of $3 \times 10^{17}$ ions cm$^{-2}$. Synchronization of the target bias and vacuum arc pulses ensured pure metal PIII without significant metal deposition. After W PIII, C$_2$H$_2$ was introduced into the vacuum chamber and RF discharge was triggered inside the vacuum chamber to ignite the plasma. In this mode, a-C thin films were deposited using plasma immersion ion implantation and deposition (PIII&D) without breaking vacuum thereby eliminating potential contamination during sample transfer. In PIII&D, the C$_2$H$_2$ plasma was also sustained by 1 kW hot filament discharge. Negative high voltage ($-20$ kV) pulses with a pulse width of 400 $\mu$s were applied to the W-implanted substrate (sample 2) at a repetitive frequency of 40 Hz. The processing time was 4 h and the a-C film thickness was approximately 0.5 $\mu$m. Sample 3 was prepared by conducting a-C film deposition directly onto the untreated steel substrate under similar PIII&D conditions as sample 2.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the composition and chemical bonding of the W ion-implanted 321 stainless steel sample (sample 1). Elemental depth profiles were acquired using argon ion bombardment at an approximate sputtering rate of 4.7 nm/min. The structures and phases in the near surface were determined by X-ray diffraction and the microstructures were evaluated by transmission electron microscopy (TEM). The structure and surface morphology of the a-C films were investigated by Raman spectroscopy and atomic force microscopy (AFM). Meanwhile, the root mean square roughness ($R_m$) of the film surfaces was determined by averaging the results obtained from five different areas.

### 3. Results

Fig. 1 displays the elemental depth profiles acquired by XPS from the steel substrate after W PIII. The tungsten profile shows a typical ‘implant-like’ Gaussian distribution, implying that

![Fig. 1. XPS depth profile of the steel substrate implanted with W ions (20 kV, 3 × 10^{17} ions cm$^{-2}$).](image)

![Fig. 2. XPS spectra: (a) C1s, (b) Fe2p and (c) W4f.](image)
pure tungsten ion implantation has been achieved. Due to its chemical affinity with carbon, a large amount of carbon is found on the substrate surface. The high-resolution C 1s, Fe 2p and W 4f XPS spectra are exhibited in Fig. 2. The W 4f spectrum reveals the W 4f 7/2 doublet corresponding to carbide-modified tungsten [9,10]. One of the two C 1s peaks centered at 283.3 eV is associated with C–W bonding [11]. The other peak at 284.4 eV indicates the presence of C–C bonding or graphitic C corresponding to sp² [12–14]. The Fe 2p peaks associated with α-Fe are observed at 720.1 eV and 706.9 eV [15–17]. According to Porte [18], the binding energies of Fe 2p electrons are affected by tungsten atoms in the vicinity so that the values are slightly lower than that of pure iron. For comparison, XRD was also performed on the untreated substrate and the results are shown in Fig. 3. Only the diffraction peaks of α-Fe can be observed suggesting that no carbide phase exists in the untreated substrate. The presence of Fe₂TiO₄ results from natural surface oxidation.

Fig. 4 depicts the microstructures of the un-implanted and W-implanted 321 stainless steels as revealed by TEM. Compared to the un-implanted sample, the micrograph of W-implanted layer shows the existence of high-density dislocations induced by high-energy ion implantation. Being large and heavy, tungsten ions introduce substantial radiation damages to the substrate surface resulting in defect strengthening.

Fig. 5(a) and (b) show the Raman spectra acquired from the a-C films deposited on the W PIII and untreated 321 stainless steel samples, respectively. By using Gaussian multipeak fitting, both Raman spectra can be deconvoluted into two subpeaks: G band at 1560 cm⁻¹ and D band at approximately 1360 cm⁻¹. Because of the same deposition conditions, the two a-C films yield similar Raman spectra, which indicate that both films are amorphous carbon. Our results show that, owing to the same preparation parameters, the two samples have similar film structures that are not modified by the different substrate surfaces.

Atomic force microscopy (AFM) was performed to study in details the surface morphology of the a-C films. Fig. 6 depicts the AFM images over a 1 μm² area on the two samples. The morphology of the a-C film on the untreated substrate resembles that of the film on the pre-implanted substrate to some extent. Nonetheless, denser buds and shallower pits are observed on sample 2 (a-C film/W-implanted steel) compared to sample 3 (a-C film/untreated steel). The root mean square roughness (Rₘ) of the film surface is also improved from 6.98 nm to 4.12 nm after the pretreatment.

4. Discussion

There are three recognized thin-film growth modes at the post-nucleation stage before the film develops a typical structure zone model (SZM) structure: (a) layer or Frank–van
der Merwe mode, (b) layer-plus-island or Stranski–Krastanov (SK) mode and (c) island or Volmer–Weber mode. The growth mode depends upon the deposited strain energy and surface energy. The growth mechanisms of the a-C films deposited by PIII&D can be explained using the statistical formation theory [19]. The growth models for the a-C films on the W-implanted substrate and without pretreatment are illustrated in Fig. 7.

The carbon ion density in PIII&D is usually less than that in other deposition methods such as vacuum arc deposition (VAD) and the formation of critical carbon nucleation sites is relatively difficult. As shown in Fig. 7(a), the carbon deposit nucleates on the substrate surface randomly or at special defect or impurity sites on the substrate surface. The nuclei then grow by the addition of carbon adatoms and their edges merge with each other, as illustrated by the island-growth mode [19,20]. In Fig. 7 (b), a modified layer, in which carbon, tungsten and other substrate elements have been mixed, is delineated from the substrate according to our XPS results. Through W implantation, tungsten carbide and C–C bonds form on the steel substrate prior to the a-C film deposition. Previous studies have shown that tungsten carbide (WC) is a very stable carbide phase with a low carbon diffusivity and high thermal stability. It has been found to be most effective in enhancing the nucleation density of diamond coatings [21]. Compared to the untreated steel substrate, the presence of graphite C can provide a relatively lattice-matched template between the substrate and

Fig. 5. Raman spectra of sample 2 (a-C film deposited on W-implanted 321 stainless steel) and sample 3 (a-C film deposited on un-implanted 321 stainless steel).

Fig. 6. AFM images: (a) a-C film on the untreated steel and (b) a-C film on W-implanted substrate.
a-C film so as to reduce the deposited strain energy and act as the precursor of film nucleation. High-energy tungsten ion implantation leads to radiation damages in the substrate surface leading to defect strengthening (Fig. 4). The defects existing on the surface can be the preferred nucleation sites, which change the film nucleation conditions after ion implantation. Consequently, the nucleation densities are dramatically improved. Subsequent growth stems from the very dense islands leading to the development of larger, more closely packed buds with a smoother film surface (Fig. 6(b)). In this case, there is some similarity to SK growth and it is different from the a-C film/untreated substrate on which they contact each other giving rise to deep valleys (Fig. 6(a)). The substantial differences between the results of the untreated substrate and W-implanted substrate with respect to the surface roughness confirm the effects of the substrate materials on the film structure and our observations are consistent with those reported by others [22].

5. Conclusion

We have investigated and compared the a-C growth modes at the post-nucleation stage with and without W pre-implantation. Even though the Raman spectra show similar structures, the growth mechanisms and surface morphologies of the two films deposited on the implanted and un-implanted substrates are distinctly different. After ion implantation, the modified surface shows the presence of WC and the C–C bonds and defects dramatically enhance the nucleation density. It is believed that the different surface chemistry results in the shifting of the post-nucleation stage from the island mode to SK mode. A smoother film with improved surface roughness is produced on the pretreated substrate under the same deposition conditions.

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