Comparative study of mechanical properties of a-C:H films produced on tungsten pre-implanted stainless steel substrate by plasma immersion ion implantation and deposition

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Abstract

Amorphous carbon (a-C) films have good mechanical properties but poor adhesion on substrates such as tool steels limits its applications. In this work, a-C films were deposited by plasma immersion ion implantation and deposition (PIII&D) on steel substrates using different pretreatment procedures. Our experiments show that a-C:H films with good adhesion strength can be produced on W pre-implanted steel substrates but this is not so on the untreated substrate or on the steel substrate with a W buffer layer. Moreover, altering the pre-implantation parameters gives rise to different distributions and amounts of W in the modified layer and they influence film growth at a later stage. The hardness, elastic properties, and adhesion strength of the deposited a-C films are also strongly affected by the pretreatment parameters. Our results suggest an alternative means to improve the mechanical properties of a-C films on steel substrate in lieu of traditional processes such as the use of an interlayer and multilayer deposition.

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1. Introduction

Amorphous carbon (a-C) thin films have 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]. Properties which affect the usefulness of the materials are the mechanical properties including hardness (H) and elastic modulus (E), tribological properties, adhesion strength between the film and substrate, and the presence of residual stress [6]. Multilayer preparation [7,8] and deposition of an interlayer such as Si, Cr, Ti and Mo [9] are two common methods to improve adhesion strength. Recently, the synthesis of adherent a-C films on a substrate pretreated by ion implantation has been reported [10–12]. In our previous studies, tungsten was chosen as the pre-implanted species to alter the surface chemistry of the steel substrate and subsequent growth of the a-C film [13]. Owing to the excellent chemical affinity between tungsten and carbon, the mixed layer with co-existing WC and C improves the mechanical properties of the films including adhesion strength and hardness [14]. In the work reported here, we conduct a systematic study on the influence of the W pre-implantation parameters on the improvement in the mechanical properties of the films, especially the adhesion strength.

2. Experimental details

Coupons of 316 stainless steels (composition in wt.%; C: 0.070, Mn: 1.460, Si: 0.720, P: 0.025, S: 0.050, Cr: 17.350, Ni: 12.410, Mo: 2.260 and Fe: balance) were cut into dimensions of 10 mm × 10 mm × 2 mm. The samples were polished and cleaned with acetone. Tungsten plasma immersion ion implantation (PIII) was carried out in a multi-purpose plasma immersion ion implanter equipped with several plasma generating tools including RF discharge, hot filament discharge, and vacuum arc metal plasma sources [15–17]. The base pressure in the vacuum chamber was 1 × 10−5 Torr. Tungsten PIII was
conducted on samples 1 to 3 using different parameters listed in Table 1. A tungsten intermediate layer is known to improve film adhesion on tool steels fabricated by magnetron sputtering [18]. Therefore, tungsten was pre-deposited on sample 4 using the pulsed filtered cathodic arc source (deposition time = 30 min; bias voltage = −200 V; W layer thickness = 50 nm). Plasma immersion ion implantation and deposition (PIII&D) was subsequently employed to deposit the a-C:H films on samples 1 to 4 as well as the untreated control sample 5 employing the same conditions. The Ar to C2H2 flow rate ratio was 5:5 (sccm).

The C2H2 plasma was sustained by 1 kW hot filament discharge and negative high voltage pulses (~20 kV) with a pulse width of 200 μs and frequency of 40 Hz were applied to the samples. The deposition time was 4 h.

X-ray photoelectron spectroscopy (XPS) was performed on a PHYSICAL ELECTRONICS PHI-5802 to determine the composition and chemical structure. Elemental depth profiles were obtained by XPS using argon ion bombardment at an approximate sputtering rate of 6 nm/min. Raman spectra excited by a 514.5 nm Ar+ laser were acquired to investigate the structure of the a-C:H films. The spectra were analyzed by Gaussian curve fitting after linear background subtraction. The hardness was obtained by nanoindentation measurements using a CSM three-sided pyramidal diamond (Berkovich) indenter with options for continuous stiffness measurement. A series of indentations was performed in the depth range from 20 nm to 180 nm. Five indents were averaged to determine the mean H value of each load to improve the statistics. The scratch resistance of the a-C:H films was assessed by a nanoscratch test performed on a Rockwell diamond indenter with 2 μm radius on the face direction in order to delaminate the films. 600 μm scratching tracks were made on the tested samples. The experiments were performed in a clean-air environment of ~45% relative humidity at an ambient temperature of 22 ± 1 °C.

![Fig. 1](image-url)

<table>
<thead>
<tr>
<th>Samples</th>
<th>W pre-implantation conditions</th>
<th>W pre-implantation conditions</th>
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<tbody>
<tr>
<td>1</td>
<td>−10 300 30 2 5×10^{17}</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>−20 300 30 1 2.5×10^{17}</td>
<td></td>
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<tr>
<td>3</td>
<td>−20 300 30 1 2 5×10^{17}</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>No W pre-implantation; W interlayer deposited by pulsed filtered cathodic arc source (time = 30 min; bias voltage = −200 V)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Untreated control</td>
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**Table 1**

Instrumental parameters used for the five samples — samples 1 to 3 (W pre-implanted); sample 4 (W interlayer deposited); sample 5 (untreated control).

**Fig. 1.** (a) Comparison of W depth profiles obtained from the steel samples implanted with W under different conditions prior to film deposition. XPS spectra acquired in the transition layer after film deposition: (b) sample 1 — 10 kV and 5×10^{13} ions cm^{-2}; (c) sample 2 — 20 kV and 2.5×10^{13} ions cm^{-2}; (d) sample 3 — 20 kV and 5×10^{13} ions cm^{-2}.
The sample surfaces were examined by optical microscopy after the test.

3. Results

XPS elemental depth profiles were acquired from the W pre-implanted substrates prior to film deposition and the mixed interfacial layers after film deposition (samples 1 to 3). The three W depth profiles in the substrates are compared in Fig. 1(a). The higher sample voltage pushes the W distribution more deeply. The W peaks are located at \( \sim 22 \) nm in samples 2 and 3 (\(-20\) kV sample bias) compared to \(7–8\) nm in sample 1 (\(-10\) kV). In spite of the differences in the bias voltages, samples 1 and 3 have a similar W fluence of \(5 \times 10^{17}\) ions cm\(^{-2}\) whereas that of sample 2 is about \(2.5 \times 10^{17}\) ions cm\(^{-2}\). After film deposition, XPS depth profiling was conducted on samples 1 to 3 to determine the film thicknesses which are \(\sim 60\) nm, \(\sim 170\) nm and \(\sim 420\) nm, respectively in spite of the same deposition process. As shown in Fig. 1(b)–(d), mixed areas with gradual compositional changes exist at the interfaces of all three samples. The pre-implanted tungsten profiles still retain the near Gaussian shape in the transition layers, but their peak concentrations decrease because of ion mixing. Despite the same negative voltage during film deposition, a wider carbon distribution is found in the substrate of sample 3 than in sample 1. This may be attributed to the excellent chemical affinity between tungsten and carbon so that carbon atoms penetrate more deeply in sample 3. The chemical states of C and W at various depths in the mixed layers in the three samples show similar transitions as illustrated in Fig. 2. As shown in Fig. 2(a),

![Fig. 2. C1s and W4f spectra as a function of sputtering depth in the transition layer in W pre-implanted samples: (a)–(b) C1s; (c)–(d) W4f.](image-url)
the C1s peak gradually broadens and shifts to lower binding energies at larger depths. Additionally, the broadened peak at larger depths can be deconvoluted into subpeaks corresponding to W–C, C–H and C–C [Fig. 2(b)]. The detailed information on tungsten is given in Fig. 2(c) and (d). In addition to the contribution of W metal (31.79 eV), a large amount of WC (31.79 eV) is observed with increasing depths.

The surface of sample 4 (W interlayer) and sample 5 (untreated steel) are also analyzed by XPS and the results are exhibited in Fig. 3. Fig. 3(a)–(c) reveals that the a-C:H film cannot be successfully deposited on the W buffer layer in this study. Due to the high energy and chemical affinity with tungsten, a large number of carbon atoms penetrate into the W layer, resulting in the formation of WC and C–C bonds but without the expected a-C:H film. On the untreated steel sample (sample 5), synthesis of the a-C:H film is also unsuccessful. When sample 5 is sputtered by Ar⁺ during our regular surface cleaning before acquiring the XPS spectra, the peaks of the substrate elements such as Fe and Cr emerge at a depth of ∼1.3 nm [Fig. 3(d)]. Based on Fig. 3(e) and (f), there does not appear to be any reaction between the iron atoms and implanted carbon in the mixed layer. In the Fe2p spectra, only the

![Fig. 3. Surface spectra of samples 4 and 5: (d)–(f) W interlayer deposited; (g)–(i) untreated control.](image-url)
707.2 eV peak corresponding to Fe2p1/2 and 720.1 eV peak arising from Fe2p3/2, both of which correspond to Fe metal, can be detected. In addition, only one symmetrical peak at 284.5 eV can be found in the corresponding C1s spectrum, implying that no Fe–C or other compositions except C–C or C–H bonds are present.

The Raman spectra obtained from samples 1 to 3 are deconvoluted into the G and D peaks and displayed in Fig. 4. It has been reported that a higher G peak position and a greater \( \frac{I_D}{I_G} \) ratio are indicators of a higher sp² concentration in carbon films [19,20]. The G band located at the highest position of 1564.37 cm\(^{-1}\) shows the largest \( \frac{I_D}{I_G} \) value of 3.5 in sample 2. The position of the G band of sample 1 is 1559.70 cm\(^{-1}\) and the \( \frac{I_D}{I_G} \) value is 1.68. The G band of sample 3 shifts to the lowest wave number of 1551.71 cm\(^{-1}\) and the \( \frac{I_D}{I_G} \) ratio declines to 1.25 implying the lowest content of sp² bonds among the three samples.

The hardness values depend closely on the film structure and thickness, as shown in Fig. 5. The results are in agreement with the Raman data. With increasing indentation depths, the hardness is affected by the substrate as well as the film. Limited by the thickness of \( \sim 50 \) nm, the enhancement appears only near the surface on sample 1. The increasing H values with depth in sample 2 stem from the soft film and hard substrate as well as the sp²-rich structure. The reverse trend is observed from sample 3.

Nanoscratch tests were employed to examine the wear behavior and adhesion strength of samples 1 to 3. The scratch test proceeds from left to right in Fig. 6 which shows the vertical penetration during the load-ramped scratch (scratch scan) and the post-scratch scan (post scan) for each film. The initial profiles on the unscratched surface of the films have been accounted for in the displacement depths. The coefficients of friction (\( \mu \)) versus normal load and depth profile are given together with the optical micrographs of the tracks. The \( \mu \) values are calculated by taking the ratio of the lateral force and normal load on the indenter [21]. At the beginning of the scratch test, the lateral force data have substantial noise indicating a stick-slip phenomenon but the \( \mu \) values become nearly constant afterwards [22].

Fig. 6(a) and (b) shows the scratch behavior of the \( \sim 60 \) nm thick a-C:H film on sample 1 scratched with a ramping load of 1–10 mN. Limited by its small thickness, abrupt changes in the post scan [Fig. 6(a)] and coefficients of friction [Fig. 6(b)] occur at position A corresponding to a depth of 60–70 nm from the surface. The results show that the scratch tip has punched through the carbon film and penetrated into the mixed layer. The positive displacements in the post scan indicate accumulation of debris in the scratch trace. The height of \( \sim 100 \) nm measured at position A further implies the total absence of the a-C:H film at a load of \( \sim 2 \) mN. The region between A and B representing the
The mixed layer of the system behaves like the transition from the film to the steel substrate. The large fluctuation in both the post scan and $\mu$ value after position B is due to the characteristics of the steel substrate. Accordingly, the exposed portion of the steel substrate can be obviously observed in the optical micrograph for a load of $\sim 2.5$ mN.

The scratch behavior of the a-C:H film on sample 2 is shown in Fig. 6(c) and (d). Being rich in $sp^2$, the film exhibits plastic deformation along the scratch length and there is a lot of fluctuation throughout the post scan. Due to the poor adhesion, the a-C:H film cracks. Moreover, small regions of film delamination even at loads below 2 mN can be observed. They can be induced by the negative displacement in the post scan. In spite of the improved thickness ($\sim 170$ nm), obvious failure manifested as tensile-type cracks in the film appears early at position A at a load of $\sim 3.3$ mN. Materials removal and formation of the surface materials on the side of the scratch are found and the phenomenon is typical of plastic deformation.

Fig. 6. Surface profiles and coefficients of friction profiles of a-C films measured from samples 1 to 3: (a)–(b) sample 1 — 10 kV and $5 \times 10^{17}$ ions cm$^{-2}$; (c)–(d) sample 2 — 20 kV and $2.5 \times 10^{17}$ ions cm$^{-2}$; (e)–(f) sample 3 — 20 kV and $5 \times 10^{17}$ ions cm$^{-2}$.
in soft materials. The large positive displacements observed in the region from 350 μm to 600 μm during the post scan represent the positions at which the tip goes over the locally delaminated film in its path. The changes in the slope of the friction coefficients marked by A and B correspond to the interfaces of the film/mixed layer and mixed layer/steel substrate, respectively.

When the load is ramped up from 1 mN to 14 mN, the a-C:H film on sample 3 with a reduced sp² content shows a behavior different from that of sample 2. In the region before position A, the film has good adhesion and recovers elastically. When the load is increased to 5 mN, an inflexion point appears in the slope of the friction coefficients, implying influence by the mixed layer beneath the film. The film blisters by partial delamination as revealed by optical microscopy during the second region between marks A and B. However, the small delaminated areas are entirely within the scratch track, suggesting that the damage is limited inside the cracks. Increasing the load further pushes the tip into the substrate giving rise to delamination and blistering. The film exhibits obvious failure at a load of ∼10 mN as indicated by upheaval of a significant portion of the a-C:H film.

In spite of the differences in the scratch resistance of samples 1 to 3, their scratch responses can be divided into three distinctive regimes corresponding to the three properties of the systems, that is, pure film, mixed layer, and steel substrate. This is especially true when the indentation results are significantly affected by the substrate whereas the nanoscratch test can isolate the mechanical properties of different portions in the system [6].

4. Discussion

The strong catalytic effect of Fe that causes inter-diffusion of carbon atoms at and near the interface [10] inhibits subsequent growth of the a-C:H film deposited directly on the steel substrate. On the contrary, new bonds such as WC formed in the W pre-implanted steel are effective in preventing carbon diffusion into the steel substrate. The good affinity between the two elements (W and C) causes in-diffusion of carbon atoms and therefore, a gradual transition layer with W–C bonds as shown in Figs. 1(b)–(d) and 2 is formed. It may also reduce the sputtering effects by the impinging ions at a high negative voltage (−20 kV). Consequently, more C–C or C–H bonds are available for film nucleation. Previous studies have shown that tungsten carbide is a very stable carbide phase with low carbon diffusivity and high thermal stability [23]. The presence of WC is able to mitigate diffusion of the dissociated carbon atoms on the surface and the formation of ordered clusters with high sp² contents. According to the XPS results, the wider mixed layer with a larger quantity of WC bonds in sample 3 is believed to be a key factor promoting the film growth. As a result, a >400 nm thick a-C:H film with improved hardness is produced. During the scratch experiments, the film on sample 1 is too thin to bear the scratch loading, yielding at a critical load as low as 2–2.5 mN. As for sample 2, the film can better protect the substrate because of its larger thickness. However, its low hardness and sp²-rich structure result in plastic deformation and film failure at a load of 3–3.5 mN. The film on sample 3 shows the best scratch behavior of the three. Due to the improved thickness and hardness, the film provides adequate resistance against loadings. Furthermore, the W–C graded layer between the film and substrate acts as a mechanically matched template providing structural continuity as well as a buffer layer to reduce the stress concentration near the interfacial zone. The propagation and development of cracks can thus be effectively reduced to minimize failure [24]. The wider mixed zone also helps to disperse the stress.

5. Conclusion

We have investigated and compared the mechanical and tribological characteristics of a-C:H films produced on the steel substrates with different pretreatment parameters. The pretreatment parameters are observed to play important roles in the characteristics of the films such as structure and thickness. Pretreatment using the proper W pre-implantation conditions favors film growth and yields better film structure, as demonstrated by the good performance in the nanoscratch and nanoindentation tests. The W–C mixed layer not only has significant effects on the formation of well-adherent a-C:H films, but also provides a graded and strong structure between the substrate and film to disperse the stress and resist delamination. Our results suggest an alternative means to improve the mechanical properties of a-C:H films on steel substrate in addition to traditional processes such as interlayer deposition and multilayer production.

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References
