Mechanical properties of tungsten doped amorphous hydrogenated carbon films prepared by tungsten plasma immersion ion implantation

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A B S T R A C T
Tungsten doped amorphous carbon films are produced on silicon (100) wafers by post implantation of tungsten ions into the a-C:H films prepared by plasma immersion ion implantation and deposition (PIII&D). The film structures are evaluated by X-ray photoelectron spectroscopy, glancing angle X-ray diffraction, and Raman spectroscopy. The surface morphology is investigated by atomic force microscopy. The mechanical properties of the films including hardness and friction coefficients of the W-implanted layer are determined by nanoindentation and nanoscratch tests. The peak concentration of tungsten reaches 27 at.% and the formation of W–C nanocrystallites is observed. The W–C nanocrystallites and C–C bondings are found to change gradually with depth. The hardness which is slightly improved after W ion implantation is affected by the W–C strengthening phase, C–C structure, and compressive stress. Owing to energetic ion bombardment, the friction coefficient is reduced on the surface of the W-implanted layer and also increases gradually towards the bulk a-C:H film. The structural continuity enables the film to remain intact during the scratch test.

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1. Introduction

Amorphous carbon films have excellent properties including high hardness, low friction coefficient, high chemical inertness, and good corrosion resistance [1–5] and are widely used as protection coatings against wear, erosion, and high temperature oxidation [6,7]. Tungsten carbide coatings are also popular but the relatively high resistance of W–C (0.5–1.1) limit their applications. W–C coatings may also experience brittle failure due to their high elastic modulus and absence of plastic compliance [8]. Recently, W doped hydrogenated amorphous carbon films have attracted attention. These films typically contain 80–90 at.% C and exhibit tribological characteristics of H:DLC with lower friction coefficients. In addition, the thermal stability and oxidation resistance of W–C is considerably better than those of H:DLC [8–11]. A variety of methods such as plasma-assisted chemical vapor deposition (CVD), magnetron sputtering and ion beam assisted deposition (IBAD) have been developed to produce W–C/a-C:H films [12]. Studies so far have indicated that in comparison with other metal doped a-C:H films such as TiC/a-C:H, it is relatively difficult to achieve carbide crystallinity at low substrate temperature [13,14]. Meanwhile, hardness improvement typically leads to deteriorated tribological properties.

Ion implantation can produce metastable layers in materials via nonequilibrium processes. In addition to providing a mechanism for the introduction of foreign elements into the matrix, ion implantation is found to predictably alter the level of disorder within the host structure thus opening up means to bring desirable changes in the surface properties to the materials [15]. In this work, acetylene (C₂H₂) plasma immersion implantation and deposition (PIII&D) was used to fabricate carbon films with better adhesion to the substrate [16,17]. Tungsten ion implantation was subsequently conducted without breaking vacuum to produce W–C/a-C:H films. The crystalline phases of tungsten carbide embedded in the amorphous carbon matrix were found to vary gradually with depths. The effects of this graded structure were investigated by determining the chemical states, microstructures and mechanical properties. The mechanical properties also exhibited gradual variations similar to the structural changes and the surface friction coefficient was reduced while the hardness was retained.

2. Experimental details

Silicon (100) wafers were pre-cleaned in an acetone bath ultrasonically and then rinsed in an ethanol bath. Film deposition...
was carried out in a multi-purpose plasma immersion ion implanter (PIII) equipped with plasma generating tools such as RF discharge, hot filament discharge, and vacuum arc metal plasma sources [18–20]. Prior to film deposition, the substrates underwent Ar+ sputter cleaning for 5 min at a base pressure of $2 \times 10^{-3}$ Pa to remove surface contaminants and surface oxide. A mixture of acetylene (C$_2$H$_2$) and argon was subsequently bled into the chamber with a constant flow ratio of 20:5 sccm and the plasma was triggered using radio frequency (RF). Film deposition was carried out at a constant RF power of 200 W. The duration was about 200 μs and the repetition rate was 40 Hz. A negative bias voltage ($-20$ kV) was applied to the substrates during deposition to improve film adhesion by ion mixing. The processing time was 2 h and the a-C:H film thickness was approximately 200 nm. The working pressure in the chamber was approximately $1.22 \times 10^{-1}$ Pa. Afterwards, tungsten PIII was conducted without breaking vacuum thereby eliminating potential contamination during sample transfer. The following conditions were used: target negative bias $V_i = -20$ kV; main arc average current $I_a = 1.0$ A; pulse repetition rate $f = 40$ Hz. The sample underwent W PIII for about an hour to achieve an approximate implant fluence of $2.5 \times 10^{17}$ ions cm$^{-2}$. Synchronization of the target bias and vacuum arc pulses ensured pure metal PIII without significant metal deposition.

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**Fig. 1.** W-implanted a-C:H film: (a) elemental depth profiles acquired from the W-implanted layer of; (b) W4f core level spectrum as a function of sputtered depth; (c) C1s core level spectrum as a function of sputtered depth.

**Fig. 2.** Evolution of the grazing incident XRD spectra of pure a-C:H film and W-implanted a-C:H film.
X-ray photoelectron spectroscopy (XPS) was performed on a Physical Electronics PHI-5802 to determine the composition and chemical structure of the films. The core peaks of C1s and W4f were recorded and analyzed every minute. To eliminate interferences from surface contamination and oxides, the sample was taken at almost the same depth after 2–3 nm of the surface was sputtered away by Ar ions. Raman spectra excited by a 514.5 nm Ar+ laser were acquired to investigate the structural characteristics of the carbon films. The spectra were analyzed by Gaussian curve fitting and linear background subtraction. XRD was used to investigate the crystalline phases of the thin films. The XRD analysis was performed using a Philips X'Pert X-ray diffractometer with a Cu Kα monochromatic radiation source (λ = 0.154 nm) operated at 40 kV and 40 mA. The samples were scanned for a range of 2θ from 20° to 100° in the symmetric diffraction mode for analysis of the bulk of the films as well as in the asymmetric mode (glancing incidence of 0.5°) for more surface-sensitive characterization. An atomic force microscope (AFM) made by Park Scientific Instruments/Auto Probe CP was utilized to assess the surface morphology of the a-C:H films in the contact mode. 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 were performed in the range of depths from 20 nm to 200 nm. Five indents were averaged to determine the mean H value of each load to improve the statistics. Because of the limited film thickness (~200 nm), it should be noted that the hardness can be affected by the film as well as the substrate. The adhesion and abrasion properties of the W-implanted layer were evaluated with the nanoscratch option (LFM option).

3. Results and discussion

The XPS elemental depth profile acquired from the W-implanted a-C:H film is depicted in Fig. 1(a). The W peak of 27% is located at approximately 6 nm from the surface. After the W peak (~6 nm), the W concentration decreases gradually with increasing carbon contents. As shown in Fig. 1(b), with increasing sputtered depth, the W-implanted layer displays a gradual structural change manifested by the intensities of the two sub-peaks assigned to W–C bondings. The C1s core level spectrum in Fig. 1(c) shows a broadened peak on the surface which can be resolved into three sub-peaks located at 283.1 eV, 284.2 eV and 285.1 eV that correspond to tungsten carbide, graphitic carbon and disordered carbon, respectively [21–22]. The C1s spectrum shifts to the higher binding energies with depths indicating reduction in the W–C and graphitic carbon contents. The structural changes observed from the W-implanted a-C:H are confirmed by the GIXRD spectra in Fig. 2. Compared to the amorphous carbon film, the newly formed peak broadening between 53–57° is attributed to a nanocrystalline WC1−x (200) phase, and the other two narrower peaks suggest the presence of larger particles of WC1−x (211) and W–C (102), respectively [21,23].

The Raman spectra in Fig. 3 also show the structural change in the a-C:H film after W ion implantation. After implantation, the total Raman scattering intensity (peak height) decreases markedly because of the formation of a centrosymmetric phase W–C that is inactive to

![](image1.png)

**Fig. 3.** Raman spectra of pure a-C:H film and W-implanted a-C:H film.

![](image2.png)

**Fig. 4.** AFM images and RMS roughness values of (a) pure a-C:H film and (b) W-implanted a-C:H film.

![](image3.png)

**Fig. 5.** Nanohardness of pure and W-implanted a-C films as a function of indentation depths from 20 nm to 200 nm.
Raman excitation. The G-peak position of the implanted film shifts from 1543.5 to 1555.6 cm\(^{-1}\). It is known empirically that a higher wavenumber of the G-peak position arises from a larger graphitic component. It can be further demonstrated that the higher intensity of the D peak relative to that of the G peak can be attributed to the disorder activated optical zone-edge phonons. This increase has also been previously correlated to an increase in the sp\(^2\)/sp\(^3\) bonded carbon in the film [23]. The improved sp\(^2\) fraction may stem from energetic ion bombardment that graphitizes the film and promotes the growth of sp\(^2\) bonded carbon.

Fig. 4 depicts the AFM images acquired from a 5 \(\mu\)m\(^2\) area on the two samples. Compared to the smooth morphology of the untreated a-C:H film, the W-implanted sample has apparent spikes indicative of the formation of W–C nanocrystallites. The root mean square roughness \((R_{\text{rms}})\) of the film surface also rises from 0.765 nm to 2.83 nm after W implantation.

As shown in Fig. 5, a slight hardness enhancement results after W implantation. Though tungsten carbide is known as the strengthening phase and confirmed to be present in the implanted a-C:H film, the increasing contents of sp\(^2\) bonding may weaken this strengthening effect resulting in the limited improvement in hardness. Nanoindentation is adopted to investigate the influence of W implantation with the maximum normal displacement of \(-120 \text{ nm}\). Fig. 6 illustrates that the friction coefficient is lower on the W-implanted layer. According to the depth of the normal displacement, the friction efficient increases gradually from \(-0.07\) on the surface to \(-0.17\) in the interior of the a-C:H film and no abrupt change is observed, thus indicating that the variation is not due to failure in the film.

Wadson et al. [24] have directly observed the multiple charge states of W ions (W\(^\text{+}\) to W\(^{6+}\)) with various incident energies (20 to 120 keV) result in a large amount of dislocations and severe damage along a relatively long incident track as demonstrated in Fig. 7(a). The majority of the damage resides in the near surface and it diminishes with reduced tungsten concentration. The defects may constitute the preferred nucleation sites beneficial to the formation and growth of the W–C nanocrystallites [Fig. 7(b)]. The gradual change in the chemical composition in the implanted region causes variation in the properties of the film. The hardness depends on the strengthening tungsten carbide phase and C–C bondings. Though graphitization results in higher contents of sp\(^2\), the stress induced by ion implantation neutralizes the weakening effect leading to limited improvement in the hardness. On the other hand, the nanocrystalline phase produces compaction from the surface reducing film porosity which is identified as a source of mechanical weakness. With regard to the friction coefficient of the film, the excellent tribological properties rendered by the graphitic structure improve the resistance during the scratch test. The damaged surface with higher graphitization is corroborated by the shift of the C1s core level XPS results. Self-lubrication of the graphite structure reduces the friction coefficient to less than 0.1 on the surface. Meanwhile, the structural continuity enables the film to remain intact during the scratch test.

4. Conclusions

Formation of W–C nanocrystallites in the a-C:H matrix can reduce the brittleness and increase the hardness offsetting the relatively high un lubricated friction coefficient of W–C which is a drawback and limits the overall performance of W–C:H films [6]. In this work, W doped a-C:H films are successfully fabricated by W ion implantation after fabrication of the a-C:H films by PIII&D. W ion implantation yields graded transformations in both the structure and properties of the films. As a result of the compressive stress induced by ion implantation and formation of the W–C strengthening phase, the hardness is enhanced slightly in spite of graphitization in the film. Meanwhile, the self-lubricating feature provided by the graphite-rich structure offsets the negative effect of W–C in the scratch test. The friction efficient is thus reduced to below 0.1 on the surface. The gradual change in the structure and properties can be explained by the damage and chemical effects of ion implantation. Our results suggest an alternative means to produce W doped amorphous carbon films with improved hardness and scratch resistance.

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