Magnetron-sputtered nc-TiC/a-C(Al) tough nanocomposite coatings

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Abstract

Amorphous carbon (a-C) deposited via magnetron sputtering usually has high residual stress, thus deposition of thick coating is difficult. In this study, aluminum was doped into a-C by co-sputtering of graphite and Al targets to drastically reduce the residual stress and enhance the toughness but at certain expense of hardness. To restore the hardness, TiC was embedded in the a-C(Al) matrix in the form of nano-sized crystals. The resultant coating is a thick nanocomposite of nanocrystalline TiC imbedded in amorphous carbon matrix doped with aluminum, or, nc-TiC/a-C(Al). Under the experimental conditions studied, the 3-μm-thick nc-TiC/a-C(Al) coating exhibited moderately high hardness (about 20 GPa) but coupled with very high toughness (55% of plasticity during indentation deformation), and very low residual stress (0.5 GPa).

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1. Introduction

For decades, diamond-like carbon or amorphous carbon (a-C) has attracted a great deal of research attention and already found itself in a whole range of engineering applications owing to its excellent tribological properties such as high hardness, good wear resistance and low friction when sliding against most engineering materials in various lubrication environments [1,2]. Amorphous carbon can be produced by various techniques from various sources of carbon [3]. Comparing to hydrogenated a-C (or a-C:H), in which hydrocarbon gases were employed as the source of carbon, hydrogen-free a-C exhibits more beneficial properties such as higher hardness and elastic modulus, lower friction in humid environment, higher thermal stability, etc. [4]. However, one of the big drawbacks of magnetron sputtered hard hydrogen-free a-C coatings is its high residual stress acquired during deposition process, which limits the coating thickness and adhesion strength thus limits its applications. For instance, Hou and Gao [5] reported that hydrogen-free a-C film deposited by pulsed laser deposition peels off as the coating thickness exceeds 200 nm. Hydrogen-free a-C film deposited by Filtered Cathodic Vacuum Arc delaminates from the substrate at thickness about 180 nm [6]. Mounier and Pauleau [7] noted that sputtered a-C deposited at −50 V bias cannot adhere to Si substrate if the coating thickness exceeds 1 μm. This also happens in hydrogenated a-C deposited by chemical vapor deposition (CVD). Ham and Lou [8] deposited a-C:H coatings by r.f CVD and concluded that an a-C:H film of more than 2 μm in thickness is too stressed to adhere well to most substrates. Depending on the structure, residual stress of a-C ranges from a few GPa to 10 GPa [9–11]. To overcome this problem, composition-graded intermediate layers [5,12], annealing [13], and doping with metallic or nonmetallic elements [14,15] have been applied. Annealing may affect microstructure of the substrate, which limits the choice of substrate. Recently, we proposed bias-graded deposition [16], whereby during the deposition process, the bias voltage was applied to the substrate in a “graded” manner from nil to a maximum value as the deposition progressed and coating thickness increased. The result was a coating of high adhesion with a graded hardness: lower at the coating–substrate interface, higher while into the coating, and highest at the coating surface. The incorporation of metals into hydrogen-free a-C matrix is another effective way in reduction of residual stress. However, hardness of
the coating suffers too much: about 60% of the coating hardness was lost when it was doped with only 10 at.% of aluminum [17].

The quest for high hardness in a material probably dates back in history to ancient times. In modern times, Hall–Petch law described the relationship between increase in hardness and the decrease in grain size. As the grain size falls down to nanometer range, as small as a few nanometers to tens of nanometers, the operation of dislocations is hindered [18] thus hardness sharply increases. In a nanosized material, deformation materializes through grain boundary sliding [19]. If grain boundary sliding is also restricted by limiting the intergrain spacing, then a superhard material becomes possible. Imbedding hard grains of 3–4 nm in diameter into a hard amorphous matrix (with about 1 nm of grain separation) thus produces nanocomposite coatings of superior hardness (for example, 80–100 GPa) [20,21].

However, the superhard coatings lack the toughness because the plasticity is suppressed. Toughness of hard coatings can be enhanced if grain boundary sliding is facilitated by increasing the intergrain separation coupled with random orientation [22], i.e. high angle grain boundaries to minimize incoherent strain and facilitate many nanocrystalline grains to slide in amorphous matrix to release strain and obtain high toughness. This, of course, will inevitably cost some hardness. Another way of improving toughness in a hard nanocomposite coating is to imbed the nanocrystalline hard phase in the matrix of a soft metal [19], which, in fact, is a kind of “miniaturization” of the same methodology used in making cermets (composites made of ceramics and metals) [23].

In this work, we produce “medium hard” but tough matrix by doping Al in amorphous carbon, and co-sputter to imbed in it a hard and randomly orientated nanocrystalline phase. This coating is expected to have low residual stress (thus can be made thick), high hardness and toughness. Since the carbon in the matrix continues to contribute to the low friction and good wear resistance, this coating should have great potential for engineering applications.

2. Experimental details

2.1. Coating preparation

The deposition was carried out at the E303A magnetron sputtering system (Penta Vacuum-Singapore). Details of the deposition system had been described elsewhere [24]. Graphite (99.999% purity), Ti (99.995% purity), and Al (99.995% purity) targets were located about 100 mm above the Si(100) substrate. From mono- or multi-target co-sputtering, four kinds of coatings were deposited: a-C, a-C(Al), TiC/a-C, and TiC/a-C(Al). For all samples, a bias voltage of −150 V was applied and the power density of graphite target was kept constant at 10.5 W/cm². Power density of metal targets was varied for desirable composition. The base pressure of the deposition chamber was pumped to $1.33 \times 10^{-5}$ Pa and the process pressure was kept constant at 0.4 Pa with 50 sccm Ar flow. The substrates were ultrasonically cleaned for 20 min in acetone followed by 10 min ultrasonic cleaning in ethanol prior to be introduced into the vacuum chamber. After loading, the substrates were heated to and maintained at 150 °C for 20 min before plasma cleaning for 30 min at RF induced bias voltage of 300 V to remove possible oxides and contaminants on the surface. During deposition, the substrate temperature was maintained at 150 °C.

2.2. Coating characterization

Coating thickness was measured using profilometer (Dektak 3SJ) through a sharp step created by masking part of the substrate. Structure of the coating was investigated with a Renishaw Raman spectroscope at 633 nm line excited with a He–Ne laser and X-ray diffraction (XRD, Philips PW 1830) with Cu K$\alpha$ X-ray source at wavelength of 0.15406 nm. Additional structural characterization was performed by transmission electron microscope (TEM) using JEOL 200 kV system. Thin films of about 30 nm in thickness were deposited on potassium bromide pellets and then the pellets were dissolved in deionized water to float off the coating for TEM study. Coating chemistry was analyzed with X-ray photoelectron spectroscopy (XPS) using a Kratos–Axis spectrometer with monochromatic Al K$\alpha$ (1486.6 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer. The base vacuum of the chamber was $2.66 \times 10^{-7}$ Pa. The survey spectra in the range of 0–1100 eV were recorded in 1 eV step for each sample followed by high-resolution spectra over different elemental peaks in 0.1 eV step, from which the composition was calculated. Curve fitting was performed after a Shirley background subtraction by nonlinear least square fitting using mixed Gauss–Lorentz function. Hardness measurement was conducted with a Berkovich diamond indenter (Nanoindenteter XP). The hardness was determined by continuous stiffness measurement [25]. The indentation depths were set not to exceed 10% of the coating thickness to avoid possible substrate effect. Also, from the loading and unloading curves, the plasticity was estimated by dividing the residual displacement after complete unloading with the maximum displacement. The residual stress was obtained from change in the radius of curvature of the Si wafer measured before and after deposition by a Tencor laser scanner. The stress values were calculated using the well-known Stoney’s equation

$$
\sigma = \frac{E_s}{6(1 - v_s)} \frac{t_c^2}{t_x} \left( \frac{1}{R_2} - \frac{1}{R_1} \right)
$$
where \( E_s/(1 - \nu_s) \) is the substrate biaxial modulus (180.5 GPa for Si(100) wafers [26]); \( t_c \) and \( t_w \) are wafer and coating thickness; \( R_1 \) and \( R_2 \) are the radius of curvature of Si wafer before and after deposition of coatings, respectively.

3. Results and discussion

Ignoring the 2–10 at.% of oxygen at the surface, the coating composition was tabulated in Table 1. Also put in Table 1 are the thickness, \( I_D/I_G \) ratio, nanoindentation hardness and residual stress. XPS spectra (Fig. 1) show C 1s (284.6 eV) peaks from amorphous carbon matrix, its chemical shift at 281.8 eV as in TiC [27], and Al 2p peaks at 74.2 eV [15]. Aluminum carbide has a binding energy at 281.5 eV and aluminum oxyxcarbide has a binding energy at 282.5 eV [28], which are within the spread of the C 1s peak for TiC. However, comparing the two profiles of nc-TiC/a-C and nc-TiC/a-C(Al), the peak shapes do not have noticeable difference. As such, it is believed that the Al doped goes to the a-C matrix.

Fig. 2 shows the XRD spectra of Al-doped amorphous carbon (a-C(Al)), nanocrystalline TiC imbedded in amorphous carbon (nc-TiC/a-C), and nanocrystalline TiC imbedded in Al-doped amorphous carbon (nc-TiC/a-C(Al)). The a-C(Al) profile does not have noticeable peaks except the Si substrate peak at around 69°2θ. In nc-TiC/a-C, the nc-TiC grains are mostly oriented along [111] and [200] crystal directions. Thus there is no preferred orientation of TiC crystalline phase in the coatings [27,29]. As the a-C matrix was doped with Al, one more orientation ([220]) appears, possibly because aluminum doped lowered the crystal formation energy on the (220) plane. Also note that the peak intensities and the widths at all the orientations are almost the same, indicating uniform grain size and random orientation. Ignoring the microstraining effect (which affects the XRD peak width), as a first-order approximation, the average crystalline size can be estimated by the Debye–Scherrer formula [30]:

\[
D = \frac{K\lambda}{\beta \cos(\theta)}
\]

where \( K \) is a constant (\( K = 0.91 \)), \( D \) is the mean crystalline dimension normal to diffracting planes, \( \lambda \) is the X-ray wavelength (\( \lambda = 0.15406 \text{ nm} \)), \( \beta \) in radian is the peak width at half-maximum height, and \( \theta \) is the Bragg’s angle. The calculated grain size of TiC spreads from 6 to 16 nm in the a-C matrix but within 4–7 nm in the a-C(Al) matrix. Thus doping Al in the matrix had a noticeable effect in hindering the growth of TiC nanocrystals and greatly reduced the grain size distribution. This was confirmed by TEM studies: Fig. 3(a) shows the amorphous nature of the a-C(Al); Fig. 3(b) and (c) compares the size and distribution of the nano-sized TiC. The diffraction pattern insets also confirm the random orientation of the nc-TiC (sharp rings instead of spots, and the uniform intensity of the rings instead of uneven intensity). Estimated from the TEM images using an image analyzer, the grain size of nc-TiC in a-C was about 4–14 nm and that in a-C(Al) was 3–7 nm, matching well with that estimated using the Debye–Scherrer formula (therefore, ignoring the microstraining effect was not a bad idea after all). From the TEM micrographs, the spacing between the nanograins can also be estimated. In the a-C matrix, the intergrain spacing was about 6–14 nm, while that in the Al-doped a-C is 8–15 nm, essentially the same. Since the size

![Fig. 1. XPS spectra of a-C, a-C(Al), TiC/a-C, and TiC/a-C(Al) coatings.](image1)

![Fig. 2. XRD spectra of TiC/a-C, TiC/a-C(Al), and a-C(Al) coatings.](image2)

<table>
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<th>Coating</th>
<th>C (at.%)</th>
<th>Al (at.%)</th>
<th>Ti (at.%)</th>
<th>( t_c ) (µm)</th>
<th>( I_D/I_G )</th>
<th>Hardness (GPa)</th>
<th>Residual Stress (GPa)</th>
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<td>0.3</td>
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<tr>
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<td>2.51</td>
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<td>27.0</td>
<td>1.5</td>
</tr>
<tr>
<td>TiC/a-C(Al)</td>
<td>47</td>
<td>13</td>
<td>40</td>
<td>2.73</td>
<td>3.5</td>
<td>19.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1: XPS composition and other measurements of coatings.
of the crystals is less than 7 nm, this intergranular spacing is large enough to facilitate grain boundary sliding, therefore good plasticity is expected in this coating.

Raman spectra of the coatings were shown in Fig. 4. The broad peak was deconvoluted into two peaks termed G-peak (graphite) at 1530/cm and D-peak (disorder) at 1350/cm. These peaks are characteristic for amorphous carbon and their intensity ratio $I_D/I_G$ is inversely proportional to the sp$^3$ fraction in the coating [31]. The $I_D/I_G$ ratio of a-C, TiC/a-C, a-C(Al), and TiC/a-C(Al) was measured as 1.1, 2.3, 3.3, and 3.5, respectively, which was also entered in Table 1. Evidently, addition of Ti and/or Al caused decrease in sp$^3$ fraction since the aluminum added went into the a-C matrix that disturbed the carbon structure as compared to adding titanium where Ti formed nano-sized TiC crystals with C. Compared with the pure amorphous carbon for which the $I_D/I_G$ ratio was 1.1, addition of 29 at.% Ti resulted an increase of $I_D/I_G$ by about 120%, but about 19 at.% Al going into the carbon matrix resulted an almost 210% increase in $I_D/I_G$. Addition of 13 at.% Al and 40 at.% Ti at the same time rendered almost 230% increase in $I_D/I_G$. That was a big increase in sp$^2$ bonding which helped the residual stress relaxation and promoted toughness at expense of hardness. A typical load–displacement curve of nanoindentation was plotted in Fig. 5. The hardness of the coatings thus determined was tabulated in Table 1. Not surprisingly the highest hardness (31.5 GPa) belongs to the pure amorphous carbon which has an $I_D/I_G$ ratio of 1.1. After imbedding with nc-TiC, a slight dip to 27.0 GPa of hardness occurs, again, corresponding to the increase in sp$^2$ fraction since the aluminum added went into the a-C matrix that disturbed the carbon structure as compared to adding titanium where Ti formed nano-sized TiC crystals with C.
fraction believed to come from the formation of a graphite rich layer encapsulating the nanocrystals [32]. When Al is doped in a-C, a drastic decrease in hardness is observed, as is expected from the high $I_D/I_G$ ratio (cf., Table 1), for which the lowest hardness of 8.8 GPa was recorded. Also, soft aluminum in the coating contributes to the decrease of hardness. As Ti is introduced in a-C(Al), the hardness of the composite increased to 19.5 GPa as a result of the formation of nc-TiC. So the hardness of the nanocomposite coating nc-TiC/a-C(Al) comes from the combination of the relatively hard a-C(Al) and hard nc-TiC. Since a-C was much harder than a-C(Al), it is expected that nc-TiC/a-C is much harder than nc-TiC/a-C(Al).

Since a standard test for thin film and coating toughness is not available yet, the plasticity has been used as estimation [16,24,27]. From Fig. 5, the plasticity during indentation of nc-TiC/a-C(Al) was 55%. As a comparison, the superhard (50 GPa) nanocomposite coating of nc-TiN/a-Si3N4 was almost absent of plasticity [20] while nanocomposite nc-TiC/a-C coating of hardness 30 GPa had a plasticity of about 40% and was considered “super tough” [22,27].

Another benefit of doping Al in amorphous carbon matrix is the drastic reduction in residual stress. Fig. 6 plots residual stresses of all the four coatings under study. In pure a-C, the residual stress was 4.1 GPa. After doping Ti into a-C, the residual stress experienced an appreciable decrease due to increase in sp² fraction (increase of $I_D/I_G$). After doping with Al in the pure a-C to form a-C(Al), the residual stress underwent a free fall from 4.1 to 0.3 GPa, thanks to the steep increase in sp² fraction and also to the softness of aluminum. Imbedding nc-TiC in the a-C(Al) matrix resulted negligible increase of residual stress (from 0.3 to 0.5 GPa). For amorphous carbon-based coating of about 3 μm in thickness, 0.5 GPa of residual stress is very low compared to hard coatings such as TiN, ZrN, and HfN, which could easily have a residual stress of a few GPa [33].

4. Conclusion

Multi-target magnetron sputtering was employed to co-sputter Ti, Al, and graphite to synthesize a thick nanocomposite coating consisting nanocrystals of TiC imbedded in an amorphous carbon matrix doped with Al, i.e., nc-TiC/a-C(Al). The nc-TiC/a-C(Al) nanocomposite coating achieved a very low residual stress and high toughness coupled with a medium-ranged hardness. Doping of aluminum into the amorphous matrix resulted in large increase in sp² fraction and drastic reduction in residual stress at expense of hardness. Addition of nc-TiC in the a-C(Al) matrix largely restored the hardness while the increase of residual stress was negligible. Doping of Al had a noticeable effect in hindering the growth of TiC nanocrystals and greatly reduced the spread of the grain size, resulting in much more uniform nanocrystalline TiC. Doping of Al also lowered the crystal formation energy on otherwise difficult to growth crystal orientation, like [220]. As such, nanograins of TiC form and grow in all major crystal directions (111, 200 and 220), giving rise to random orientation, which further contribute to better toughness.

Acknowledgements

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References