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Letter

Critical relative indentation depth in carbon based thin films

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Abstract

The thin film hardness estimation by nanoindentation is influenced by substrate beyond a critical relative indentation depth (CRID). In this study we developed a methodology to identify the CRID in amorphous carbon film. Three types of amorphous carbon film deposited on silicon have been studied. The nanoindentation tests were carried out applying a 0.1–10 mN load range on a Berkovich diamond tip, leading to penetration depth-to-film thickness ratios of 8–100%. The work regained during unloading (W_e) and the work performed during loading (W_t) was estimated for each indentation. The trend of unload-to-load ratio (W_e/W_t) data as a function of depth has been studied. W_e/W_t depth profiles showed a sigmoid trend and the data were fitted by means of a Hill sigmoid equation. Using Hill sigmoid fit and a simple analytical method it is possible to estimate CRID of carbon based films.

Keywords: Nanoindentation; Carbon film; Critical relative indentation depth; W_e/W_t

1. Introduction

Carbon-based thin films show wide range of mechanical properties as a function of hydrogen content, sp2–sp3 ratio, stress, density and structure [1,2]. The mechanical properties of thin film estimated by means of nanoindentation are influenced by substrate [3]. Different approaches can be used in order to remove any substrate effect [4–7], but the main approach is that the critical relative indentation depth (CRID) should not exceed 10% of the total film thickness. These approach is quick but not accurate, for instance in the case of aluminum on silicon [8]. In this work we developed a methodology that allows CRID evaluation directly from the energy response of the material during the indentation process. Special interest is given to the unload to-load work of nanoindentation, which represents the ratio between the total work (W_t) done and the recovered work (elastic) during indentation as shown in Fig. 1. It allows us to separate the indentation work into elastic (W_e) and plastic components (W_p) since $W_t = W_p + W_e$. The W_e/W_t ratio determination is straightforward from the load–unload curves. It does not need any model application and is not affected by shape of stylus, state of material (bulk or thin film) or the applied load which generally are critical for hardness and elastic modulus estimation [9]. Moreover, for carbon based coatings, W_e/W_t as function of depth have a sigmoidal trend and this trend can be fitted by sigmoid Hill equation [10]. For this reason we first study the Hill sigmoid equation to estimate CRID point under mathematical point of view. And then we apply the method developed for the W_e/W_t trend of the carbon-based films. In the end we compare the CRID points obtained with results using equation suggested by Bull to estimate CRID value in the thin film [11].

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2. Experimental details

In this experiment three types of a-C:H coatings were used [12]. The first kind of coating was deposited by sputtering

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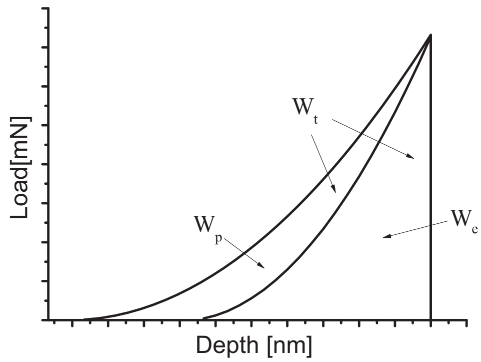

Fig. 1. Total (W_t), plastic (W_p) and elastic (W_e) works of indentation.

from a graphite target using a RF (13.56 MHz in continuous wave mode) with a thickness of ~400 nm. This was indicated as

C-1. The second kind (indicated as C-2) was deposited at the same condition but it was thicker than the C-1 (~530 nm). The third film (C-3) was deposited by pulsed plasma and the thickness of the coating was 300 nm.

The substrates for all coating was the 400 μm thick n-type Si (100). All the coatings grew at room temperature. The pressure was 0.05 Torr and an Ar/H_2 mixture gas was used.

2.1. Mechanical measurements

Film thickness was measured using a KLA Tencor P15T profilometer. The mechanical properties were measured using a CSM Nano Hardness Tester. The indentations were obtained by a three side pyramid diamond Berkovich indenter, and the Oliver and Pharr model [13] has been applied for the analysis of the data. All data reported here are average values over four measurements for each load, and the error by root mean square (rms) has also been calculated. The mechanical properties are reported as a function of indentation depth normalized to the film thickness (D). The roughness of the film surface was profiled by Atomic Force Microscopy (AFM), in contact mode with a SIS Ultra Object Instrument. For the present films, the values of roughness (Ra) are measured on an area of 5 μm × 5 μm.

3. Treatment of data

Hill equation generally describes the cooperative or non-cooperative transition from two states of a bi-component system [14,15,16]. In a heterogeneous structure composed by a coating on a substrate there are two states as well: a zone where the mechanical properties are related to the coating (C) and a zone where the mechanical properties are related to the substrate (S), and both of them are filled by n binding sites. The W_e/W_t ratio as a function of depth might then be described by a Hill sigmoid

$$y = A_1 + (A_2 - A_1)\frac{x^n}{k^n + x^n} \quad (1)$$

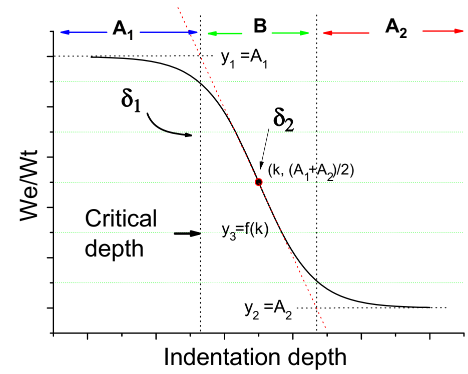

Fig. 2. Trend of Hill sigmoid equation, δ_1 is the critical relative indentation depth, δ_2 is the center of the sigmoid. A_1 is the region where the mechanical properties may be correlated only to the film, B is the transition zone, A_2 is the region where the properties are mainly due to the substrate.

where y denotes the W_e/W_t ratio, the independent variable x is indentation depth to the film thickness (D), A_1 and $A_2 < A_1$ are the upper and lower limits for y ($A_1 \le y < A_2$), and k is the abscissa of the sigmoid center. Fig. 2 graphically illustrates all of these parameters. We point out two important values named critical depths δ_1 and δ_2. The latter point δ_2 corresponds to the sigmoid center abscissa k, where y gets the value of $(A_1+A_2)/2$. On the other hand, δ_1 is the singular point near the surface indicating the boundary of the region A_1. The point δ_1 is obtained from the intersection of the straight line $y=A_1$ and the tangent to the sigmoid passing through its center, that is the point of the xy plane with coordinates $x_o=k$ and $y_o=(A_1+A_2)/2$. The slope of the tangent line at the sigmoid center is

$$\left(\frac{d_y}{d_x}\right)_{x=x_0} = \frac{(A_2 - A_1)n}{4k} \quad (2)$$

And δ_1 is obtained as the x solution of the following system of equations:

$$\begin{cases} y - y_0 = \left(\frac{d_y}{d_x}\right)_{x=x_0} * (x - x_0) \\ y = A_1 \end{cases} \quad (3)$$

After simplification one finally obtains

$$\delta_1 = k*(1 - 2/n) \quad (4)$$

Therefore, as suggested by Eq. (4), knowing only two parameters of the fit, the critical point δ_1 can be analytically determined. The A_1 represents the superficial region where the mechanical properties of the films are dominant and δ_1 is the critical relative indentation depth, CRDI. To understand if the evaluation of CRID is correctly estimated we have compared the results and the critical relative depth derived by the equation suggested by Bull [11]

$$\delta_B = 0.4\left(\frac{H}{E}\right)^{1/2} \quad (5)$$

where δ_B is the critical relative indentation depth (CRID B), H is the hardness and E is the elastic modulus.

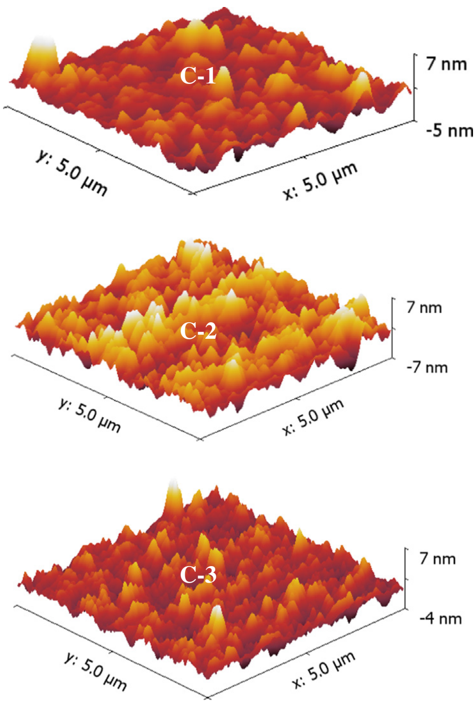

Fig. 3. Three dimensional AFM images of the carbon films, C-1, C-2, and C-3.

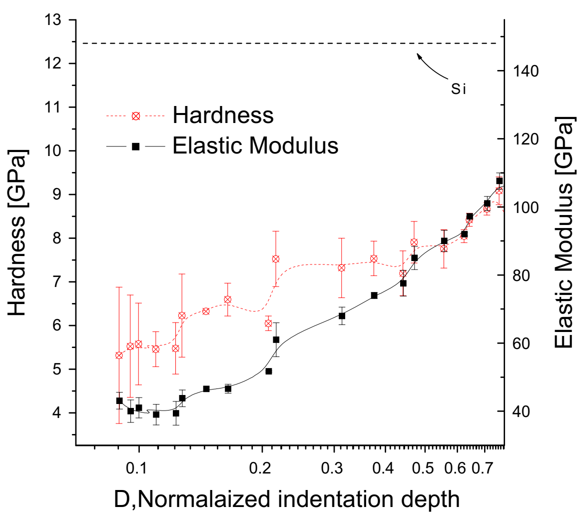

Fig. 4. Hardness and elastic modulus as a function of normalized penetration depth D for amorphous carbon film deposited on silicon, sample C-1.

4. Results and discussion

Fig. 3 shows the three dimensional atomic force microscopy images (scan area: 5 μm × 5 μm), obtained in contact mode on C-1, C-2, and C-3 surfaces. The surface of the coatings were similar and smooth, the roughness Ra varied from 3 nm to 4 nm. The substrate hardness was found as 12.1 GPa and Young modulus 160 GPa in good agreement with literature data [17]. The W_e/W_t ratio value for the substrate was found to be 0.61 in the range of loads from 0.5 mN to 10 mN. We studied the mechanical behavior of the hard a-C:H films deposited onto Si, sample C-1. In Fig. 4 the hardness and elastic modulus are represented as a function of the indentation depth normalized to the film thickness (D). For the instance of D of between 0.1 and 0.2 both mechanical properties remain quite stable ($H \approx 5.5$ GPa and $E \approx 40$ GPa). For deeper indentation they increased and went towards the substrate properties value. In Fig. 5 the W_e/W_t depth profile obtained on C-1 is plotted. It can be observed that the trend of W_e/W_t satisfactorily described by three different regions: a near surface region (A_1) where the properties may be correlated only to the film, a transition zone (B) and a third region (A_2), the deepest one, in which the properties were mainly due to the substrate and almost steady. In the zone A_1, delimited by dot line, W_e/W_t was very high around 0.83, and the in zone A_2 the W_e/W_t was 0.62 around the value estimated for pristine silicon substrate. The red straight line shows the fit based on Hill equation. Eq. (4) was used to determine the critical relative indentation depth CRID where the mechanical measurements can be related only to the film. Here, in C-1**,** CRID value was 0.14 of depth ratio. The mechanical properties were evaluated by averaging over the film influence region, from the lowest D value to δ_1, the hardness was $H = 5.81 \pm 0.49$ GPa and the elastic modulus was $E = 42.4 \pm 3.1$ GPa. The same analysis has been carried out on the sample C-2, C-3 because a similar trend of W_e/W_t ratio was found. In C-2 CRID was 0.14, the hardness was 5.79 ± 0.59 GPa and the elastic modulus 40.9 ± 3 GPa, as shown in Table 1. We estimated CRID value also for a-C: H film deposited with pulsed plasma process C-3. In this case CRID was 0.13, instead the hardness was 8.4 ± 0.4 GPa and elastic modulus was 60.8 ± 3.7 GPa. For all fits we found a good value of r^2 to be from 0.93 to 0.99, which means that the Hill sigmoid equation fits the data quite well (see Table 1). The critical relative indentation depth estimated by Eq. (4), for all coatings was around 0.14. We compared CRID with critical relative indentation depth estimated by Eq. (5), CRID B. In Table 1, CRID and CRID B are summarized. We observed that the values CRID are

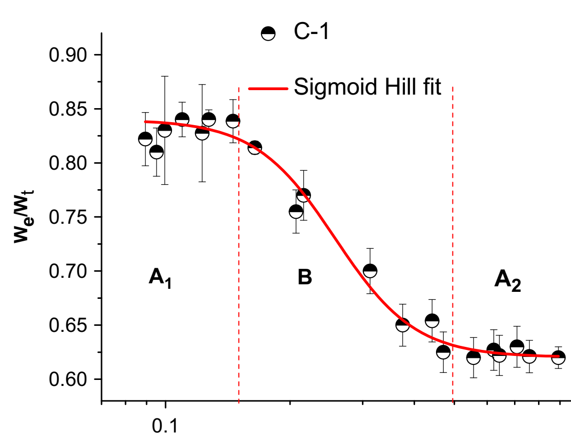

Fig. 5. Amorphous carbon film C-1 sample, unload-to-load work ratio (W_e/W_t) as a function of normalized penetration depth.

Table 1
Mechanical properties of the carbon coatings, r^2 of the Hill fit, the critical depth estimated by Hill equation and relative critical depth derivated by Bull equation.

	Hardness within CRID (GPa)	Elastic modulus within CRID (GPa)	r^2	CRID Hill equation (CRID)	CRID by Bull (CRID B)
C-1	5.81 ± 0.49	42.4 ± 3.1	0.99	0.14 ± 0.01	0.15 ± 0.02
C-2	5.79 ± 0.59	40.9 ± 3.0	0.94	0.14 ± 0.02	0.15 ± 0.02
C-3	8.4 ± 1.2	60.8 ± 3.1	0.94	0.13 ± 0.02	0.15 ± 0.02

comparable with CRID B, indicating that the analytical method developed gives reasonable estimation. The method developed to estimate CRID could be used also when hardness and elastic modulus of the carbon coatings are unclear or yet unknown before.

5. Conclusion

In this study three types of carbon films on silicon substrate were considered, the W_e/W_t ratio as a function of the normalized indentation depth was mainly studied. It has been observed that the W_e/W_t data show a sigmoidal trend. The W_e/W_t data can be fitted by means of Hill equation and the critical relative indentation depth (CRID) can be easily determined using only 2 parameters of the fit. The analytical method developed gives a reasonable estimation of CRID for film that are softer than the substrate. Moreover, it has been found that for the different amorphous carbon films on silicon substrate the CRID was around 14% of the film thickness.

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