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Determination of thin film hardness for a film/substrate system

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Abstract

A simple model for determining the film hardness for the composite hardness of a film/substrate system is developed. On the basis of volume law and current models, the model can be used without requiring any additional material property for amorphous, multicomponent and multiphase coatings. As the cause of indentation size effect (ISE) is taken into account, the ISE of the film is neglected at a high depth/thickness ratio and the introduction of Meyer's equation is avoided. The hardness values of TiC/a-C:H in situ composite films by PECVD are assessed with the model by controlling the film thickness and indenting under fixed loads, the results obtained for the films coated on Si(100) and Corning 7059 are 1479 and 1681 kg/mm^2 respectively. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Thin hard coatings deposited by CVD or PVD methods have been studied extensively during the last decade, such as TiN, alumina etc. In addition to these monolithic coatings, new coating materials such as metastable, multicomponent and multiphase coatings have been developed to fit the ever-increasing demands in coating performance. For example, (TiAl)N films with switchable Ti/Al ratio are synthesized by various methods, which are harder than TiN and have a better oxidation resistance at high temperatures; Amorphous diamond-like carbon film with sp^2 and sp^3 C–C bonding is thought to be more preferred in some applications than diamond film. As a simple and direct measurement, indentation hardness is often used as an initial guide line for the suitability of a coating for any application requiring wear resistance. However, to obtain an absolute or true hardness value for a thin film which is not influenced by the substrate, the film thickness must be generally 10 times greater than the indentation depth [1], and this restriction becomes more severe for a hard film on a soft substrate. A nanoindentation testing method is used to overcome this restriction, but this method is very sensitive to the surface roughness of the specimen tested, to any external vibration sources, and a careful calibration is required for each new indentation tip.

Instead of the direct measurements, a set of indirect methods are developed to estimate the true hardness of thin film. In these methods, a microindentation testing method is used and the composite hardness influenced both by film and substrate is measured, then the film and the substrate contributions are distinguished through various models. Buckle [2] proposed that the composite hardness H_c of a bilayer material should be expressed as a weighed sum of the different layers, in a thin film system, the H_c is given by:

$$H_C = aH_f + bH_s \tag{1}$$

with $a+b=1$.

Jonsson and Hogmark [3] proposed a geometrical approach to separate the substrate and coating contributions to the composite hardness. Based on the hypothesis that the film cracks but does not densify or get thinner during indentation, and the deformation of film is confined around the impression, the model of Jonsson and Hogmark (JH) is expressed as

$$H_C = \frac{A_f}{A}H_f + \frac{A_s}{A}H_s \tag{2}$$

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A_f represents the area on which the film mean pressure H_f acts and A_s is the area on which the substrate mean pressure H_s acts and the total area is then $A = A_f + A_s$. The model leads to the formula

$$H_C = H_S + \left[2C\frac{t}{D} - C^2\left(\frac{t}{D}\right)^2\right](H_f - H_S) \quad (3)$$

where t is the film thickness, D is the indentation depth, $C = \sin^2 f$(version 1) or $C = 2\sin^2(f/2)$ (version 2 for very hard and brittle films), and f is the angle of the tip sides with the surface ($f = 22^\circ$ for Vickers indenter). The JH model is simple and is thought to be partially successful, but the indentation size effect (ISE) has been neglected as the microhardness tester is employed.

The volume law of mixtures model is firstly suggested by Sargent [4] to describe the composite hardness. Considering the volume ratio of deformation, the basic form is as follows:

$$H_C = H_f\frac{V_f}{V} + H_S\frac{V_S}{V} \quad (4)$$

And the model is further improved by Burnett et al. [5–7] by introducing terms about ISE and so-called interface parameter χ into the relation:

$$H_C = \frac{V_f}{V}H_f + \frac{V_S}{V}\chi^3 H_S \quad (5)$$

and χ is given by

$$\chi \propto \left(\frac{E_f H'_S}{H'_f E_S}\right)^{n/2} \quad (6)$$

where E is Young's modulus and H' is hardness. The ISE is incorporated by replacing the H_s and H_f with the following equation (Meyer's law)

$$H = q\ d^{n-2} \quad (7)$$

where q is a constant, d the indentation size and n the ISE index.

As mentioned by researchers [5–10], it is very difficult to predict the deformation behavior of a film/substrate system during indentation. That is due to the complexity of the three-dimensional stress state, the different elastic and plastic properties of the film and the substrate, etc., especially in a wide D/t range. So the models listed above are further modified by some researchers, leading to more complex formula and methods [8–10]. In most of the approaches, the cause or explanation of ISE is not concerned and the Meyer's equation, which is derived from bulk materials, is employed . However, in a bilayer system, ISE should be thought as a noise factor on composite hardness calculation as different indentation loads are used, and is difficult to identify. It is important that before the ISE is introduced to the approach, the cause of ISE must be taken into account first. Unfortunately, the causes of ISE are not clearly understood and elastic recovery of impression, surface layer and measurement errors are mentioned as important factors. Bull et al. [11] implied that ISE behavior seems to be a fundamental deformation response which is independent of the additional effects like surface hardened layer or chemical surface artifacts, they also implied that the measured effect is often far larger than the explanation of measurement errors can allow. A quantitative model based on the account of recovery of elastic deformation was proposed by them to explain the ISE and fits the observed experimental data well.

On the other hand, except the JH model, assumption of some material properties, including Young's modulus, hardness and ISE index of coating, is necessary for most of the models. However, as some of these properties are parameter dependent, it can be difficult to determine for some cases like amorphous, multicomponent and multiphase coatings.

Based on the models developed, the aim of this work is to develop a new approach without assumption of material properties. Most of the current models are derived trying to estimate the ratio of plastic deformation volume for film and substrate in a wide D/t range by changing indentation load with a fixed film thickness. It is a complicated problem to construct a model apparently, and some researchers [10] implied that different physical phenomena occur during the various stages of the indentation process, therefore, a model applied to a wide D/t range seems not to be necessary.

2. The model

This new approach is also based on volume law of mixtures for the plastic zone. As the complexity of the deformation behavior is taken into account, direct prediction of the plastic deformation volume ratio is avoided and the basic model is applied in a simple form:

$$H_C = (1 - x)H_S + xH_f \quad (8)$$

which is similar to the Buckle's model. According to the result shown in a previous study [8], as the indentation load is fixed, a function near linear can be constructed experimentally between the composite hardness value and film thickness, when the D/t is within a range of 5–10 or higher. In other words, the x value will be proportional to film thickness t when the contribution of film in composite hardness is relatively low and x can be replaced by rt (r is a multiplication factor) in the above model and then

$$H_C = (1 - rt)H_S + rtH_f \quad (9)$$

which is rearranged as follows

$$H_C = H_S + rt(H_f - H_S) \quad (10)$$

However, as the influence of the film/substrate interface is taken into account Eq. (10) can be modified as

$$H_C = H'_S + rt(H_f - H_S) \quad (11)$$

where $H_s' = H_s + C_i$ and C_i is an interface factor, then the slope of the H_c vs. t plot is r ($H_f - H_s$) where r and H_f are unknown.

As indentation load is varied, H_s measurement will be changed due to ISE and r is also changed which leads to a different slope. Because the D/t ratio is high, the influence of film on composite hardness is relatively low, and the ISE is not significant to the film. When 50 and 100 g loads are used, the ratio of slope is

$$\frac{r_{100\ g}(H_f - H_{S,100\ g})}{r_{50\ g}(H_f - H_{S,50\ g})} = \frac{\text{slope}_{100\ g}}{\text{slope}_{50\ g}} \quad (12)$$

For the ratio of r, as the t/D ratio is low, the form of JH model [Eq. (3)] is approximated as follows:

$$H_C = H_S + 2C\left(\frac{t}{D}\right)(H_f - H_S) \quad (13)$$

which is similar to Eq. (11), so let r be $2C/D$, and Eq. (12) can be rearranged as

$$\frac{(H_f - H_{S,100\ g})}{(H_f - H_{S,50\ g})} = \frac{\text{slope}_{100\ g} \times D_{100\ g}}{\text{slope}_{50\ g} \times D_{50\ g}} \quad (14)$$

Therefore, H_f is the only value unknown experimentally and can be obtained by measurement and calculation.

Film texture is another factor which should be considered which will make the mechanical properties of the film anisotropic. In this study, it is assumed that the film texture is independent from the substrate and film thickness.

3. Experimental

TiC/a-C:H composite coatings were deposited on Corning 7059 glass and Si wafer substrates using the plasma enhanced chemical vapor deposition (PECVD) method. A 13.56 MHz r.f. generator is used with capacitively coupled parallel electrodes which were 12 cm in diameter with a separation distance of 6 cm, the substrates were placed on the lower electrode which had the r.f. power applied to it while the upper electrode used as gas shower was grounded. The substrates could be heated up to 600°C by a graphite heater beneath the lower electrode and the $TiCl_4$, CH_4,H_2 and Ar gas mixtures were used as the feedstocks. The film thickness was controlled by deposition time.

Micro-Vickers testing was performed at 50 and 100 g loads with a dwell time of 15 s. More than five indentations were made for each load and the average value of film hardness was calculated. The film thickness was measured by an α-step equipment with 5 nm vertical resolution. Crystal structures were analyzed by X-ray diffraction (XRD, Cu K_α), and ESCA as well as Raman spectra were employed to analyze the bond structure of films.

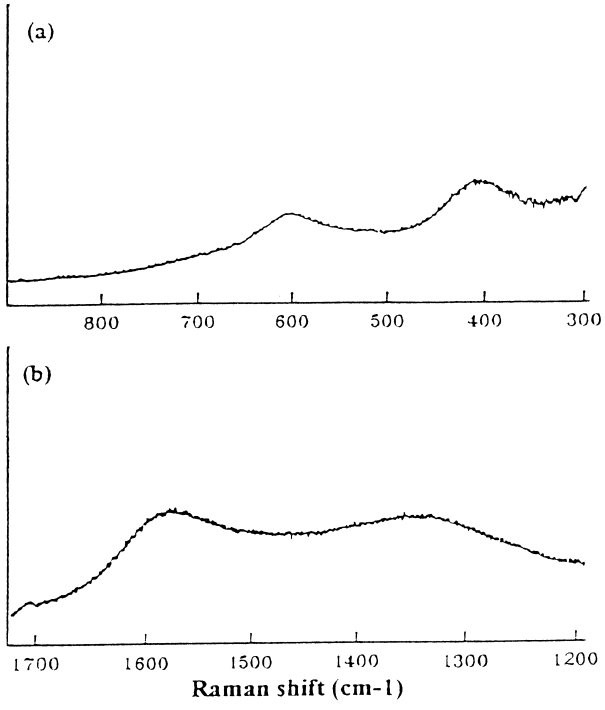

Fig. 1. The Raman spectra of (a) TiC and (b) a-C:H in the composite coating.

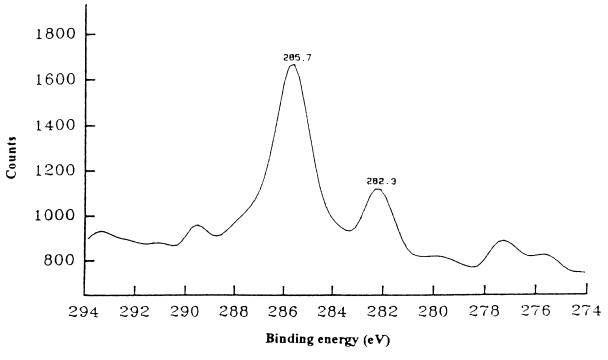

Fig. 2. The ESCA spectrum of C1s in the TiC/a-C:H composite coating.

4. Results and discussion

The as-deposited films are TiC/a-C:H composite coating [12]. Crystalline TiC phase was determined by XRD and, as shown in Fig. 1, the Raman shift of TiC and amorphous carbon bonding appear in Raman spectra at the same time which indicate that the two phases were co-deposited in PECVD system. The ESCA spectra of C1s, as shown in Fig. 2, are used to confirm the above results. The C–C (285eV) and C–Ti (282eV) are identified, and the phase ratio is quantified by peak-fitting of the spectra and can be controlled by changing the argon/methane gas ratio when methane/$TiCl_4$ ratio is fixed. The growth rate of the composite coating on Si(100) and Corning 7059 is similar with the deposition parameters listed in Table 1. The results of the micro-Vickers test with 50 and 100 g loads are shown in Figs. 3 and 4 for Si wafer and glass samples, respectively. For the D/t ratio is high, the predicted linear relation between H_c and t is achieved which shows the model is feasible in this system. The measured hardness values for the bare substrates and the measured values for the coated samples are listed in Table 2 in which H_f values are also calculated. Without intro-

Table 1
Deposition conditions for the TiC/a-C:H films synthesis

R.F. power	150W
Temperature	500°C
H_2 main gas	50 sccm
H_2 carrier gas	200 sccm
CH_4 gas	40 sccm
Ar gas	100 sccm
$TiCl_4$ bubbler temp.	40°C
Time	5–20 min

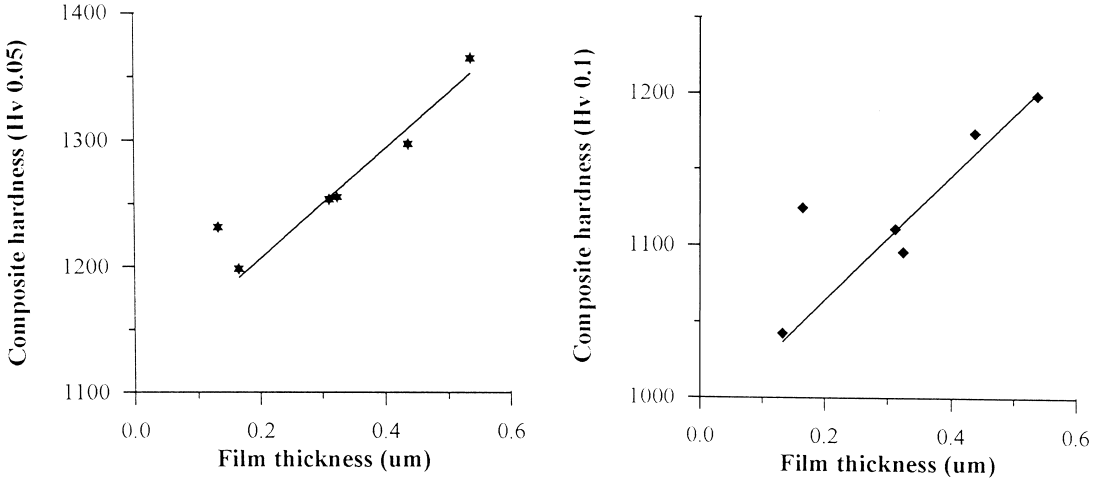

Fig. 3. The linear dependence of composite hardness on thickness of TiC/a-C:H film deposited on Si(100).

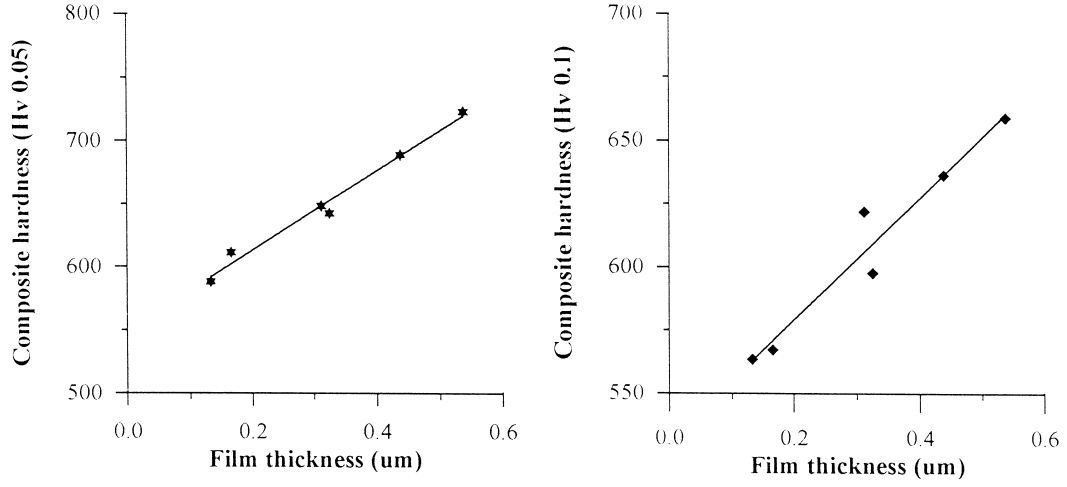

Fig. 4. The linear dependence of composite hardness on thickness of TiC/a-C:H film deposited on Corning 7059.

Table 2
Results of the microhardness tests and calculation

Substrate	Load (g)	Slope ($\times 10^3$kg/mm^3)	H_s (kg/mm^2)	D (um)	H_f (kg/mm^2)
Si (100)	100	405.61	1033.9	1.85	1478.7
	50	435.97	1122.2	1.22	
Corning 7059	100	240.41	559.9	2.44	1681.4
	50	318.17	671.6	1.66	

ducing any assumed value of material properties, the film hardness is accessed as 1479 and 1681 kg/mm^2 for Si (100) and Corning 7059 samples respectively by the composite hardness model. The deviation for the calculated film hardness value is around 6.5% between different substrate as mean value (1580 kg/mm^2) is considered. The difference may come from fitting model simplification, like assumption of volume law, interface effect, film texture and ISE, or deviation from measurement.

For the approach proposed in this work, the model can not be applied unless the linear relation between H_c and t is constructed with a high D/t ratio, and the influence of some noise factors from measurement can be avoided when the slope value is used as the basis of calculation. As mentioned above, if the influence of the effect can not be identified precisely, the ISE is also a noise factor in a bilayer system for hardness assessment especially when the D/t ratio is low, but the effect is neglected or is introduced into the model with Meyer's equation in current approaches, however, the ISE of thin film for composite hardness is not apparent and can be neglected in this model as D/t is high. Furthermore, this simple model does not require additional material properties, such as Young's modulus and ISE index, which makes it difficult to use some of the current models for amorphous, multicomponent and multiphase coatings.

5. Conclusion

A simple model without requiring any additional material property is developed on the basis of volume law and current models to determine the film hardness from the composite hardness of film/substrate system measured by a microhardness tester. The hardness values of TiC/a-C:H insitu composite films by PECVD are assessed with the model by controlling the film thickness and indenting at fixed loads, the results obtained for Si(100) and Corning 7059 are 1479 and 1681 kg/mm^2 respectively.

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