Comparison of two models of thin diamond film microhardness data to predict the hardness of CVD diamond

Alex M. Cock* and Nicola M. Everitt**
Department of Aerospace Engineering, University of Bristol, Queen's Building, University Walk, Bristol, BS8 1TR (UK)
Paul W. May, Chris A. Rego, Mike N. R. Ashfold and Keith N. Rosser
School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS (UK)

Abstract

Microhardness Knoop indentation testing of diamond films (1–3 μm thick) on silicon and on a titanium alloy is reported. The measured hardness results were influenced by the substrate, and the results were modelled to give the hardness of the diamond film. Two models were used. The first was an empirical equation determined from finite element simulations of the load–displacement response of a hard film on a soft substrate. The second assumed the measured hardness to be dependent on the volume of the film and the volume of the substrate deformed. The first model gave a better fit in both cases, predicting a diamond film hardness of 112 GPa and 59 GPa for the silicon and titanium alloy substrates respectively. There is a large titanium carbide interfacial layer between the diamond film and the titanium alloy substrate, which is probably the major reason for the lower predicted hardness result.

1. Introduction

There has been great interest in diamond films since the discovery of their synthesis at reduced pressures. One of their potential applications is as hard, wear-resistant, protective coatings, as a result of diamond's exceptional properties [1].

Microhardness indentation testing is a useful technique to determine the hardness of materials. However, when testing thin films, the results are influenced by the substrate and, therefore, the data needs to be modelled to predict the intrinsic hardness of the film.

2. Microhardness indentation testing

Microhardness indentation testing is an easily accessible, simple test to perform and only requires a small sample surface area. To perform a test, an indenter of known geometry is pushed under a fixed load onto a specimen's surface. The area of the resultant impression is then measured. For the hardness measurements reported in this paper, a Knoop pyramid indenter was used, because it has a relatively high ratio of depth to long diagonal. The material's hardness (in gigapascals) is given by

$$H = \frac{P}{A} = 139.55\frac{P}{d^2} \quad (1)$$

where P is the load (in grams) and A is the contact area (square micrometres) of the residual impression. For a Knoop indenter, $A = d^2/139.55$, where d is the length of the long diagonal, which is measured optically.

However, for the intrinsic hardness of films to be determined, indentations must be made such that the stress field associated with the indentation does not penetrate through to the substrate. Conventionally, it is assumed that a ratio of the film thickness (t) to indentation depth (h) of 10 is needed for hardness results to be independent of substrate effects [2]. However, Aisenberg and Kimock claimed that $t/h \geqslant 5$ is sufficient for diamond-like carbon [3]. The ratio is most likely to be dependent on the elastic modulus of the film, *i.e.* films with higher modulus will require smaller t/h ratios.

Therefore, when testing thin films, very small indentations are required. Alternatively, the combined response of both the film and the substrate is measured using larger indentations, and the results modelled to give the film's hardness. Two models are described below, which are applied to hardness results from diamond films on a silicon substrate and from diamond films on a titanium alloy (Ti–6%Al–4%V) substrate.

One very important factor affecting all hardness results is the experimentally observed phenomena of the indentation size effect (ISE) [4]. Hardness results are

*Present address: Department of Materials, University of Oxford, Oxford OX1 3PH, UK.
**Author to whom correspondence should be addressed.

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often quoted as being load independent, which is not the case for indentations made using small loads (less than 200 g). In fact, in general, the recorded hardness increases with decreasing applied load. The ISE can be characterized by

$$P = Kd^m \tag{2}$$

where P is the applied load, d is the diagonal of the indentation, K is a material-dependent constant and m is the ISE index. The ISE is more marked in hard solids,—most ceramics have m in the range 1.6–1.9 [5] and it is extreme in natural diamond [6]. There are many factors which contribute to the ISE, including the modulus of the material tested, friction between the indenter and the material, work hardening of the material, etc. Their interrelationship is not well understood. Neither model includes corrections for the ISE.

3. Modelling hardness results

Bhattacharya and Nix [7] performed finite element calculations for the load–displacement response of a conical indenter penetrating a silicon film on an aluminium substrate. From these results, they calculated the hardness response of this composite system by analysing the unloading curves using the theory of Doerner and Nix [8]. They then determined the empirical equation for hardness with the indentation depth:

$$(H_m - H_s) = (H_f - H_s)\exp\left\{-\frac{H_f/H_s}{\sigma_f/\sigma_s(E_f/E_s)^{1/2}}\frac{h}{t}\right\} \tag{3}$$

where H is the hardness, σ is the yield stress, E is Young's modulus, t is the film thickness and h is the indentation depth. The subscripts f, s and m refer to the film, the substrate and the measured quantity. A similar equation was found for an aluminium film on a silicon substrate.

Equation (2) can be rewritten as

$$\ln(H_m - H_s) = \left\{-\frac{H_f/H_s}{\sigma_f/\sigma_s(E_f/E_s)^{1/2}}\frac{h}{t}\right\} + \ln(H_f - H_s) \tag{4}$$

Thus, plotting $\ln(H_m - H_s)$ against h/t should result in a straight line with intercept $\ln(H_f - H_s)$ and gradient $-(H_f/H_s)/[(\sigma_f\sigma_s)(E_f/E_s)^{1/2}]$. Hence, if the substrate hardness is known, then the film hardness can be calculated from the intercept. Also, if the other substrate properties and either the yield stress or the modulus of the film are known, then the other parameter can be calculated from the gradient.

The finite element code used by Bhattacharya and Nix has since been improved by Laursen and Simo to account for pile-up and sink-in around an indentation [9]. Furthermore, the Doerner and Nix analysis of unloading curves has been improved by Oliver and Pharr [10]. Hence, eqn. (3) should be checked against newly calculated load–displacement curves.

Sargent initially proposed the second hardness model used [10a]. The measured hardness is given by a weighted average of the hardness of the film and that of the substrate. The weightings are determined by the volume of plastically deformed material in the film (V_f) and in the substrate (V_s). This model was subsequently modified by Burnett and Rickerby to include an empirically derived parameter χ^3, which accounted for the deviation in plastic zone size from ideal geometry [11]. Sargent's equation became

$$H_m = \frac{H_f V_f + \chi^3 H_s V_s}{V_f + \chi^3 V_s} \tag{5}$$

Burnett and Rickerby approximated χ to be

$$\chi = \left(\frac{E_f H_s}{H_f E_s}\right)^n \tag{6}$$

where n was found empirically to be of the order of 0.3–0.5.

Fabes *et al.* adapted eqn. (5) to take account of whether the indenter's stress field is entirely contained within the film, and applied this to results obtained from low load, depth sensing indentation (nanoindentation) [12]. They assumed the plastically deformed volumes to be a 45° triangular cone, arguing that the specific shape is unimportant as the volume terms appear as both numerator and denominator terms. The radius of the cone is calculated from the contact area using the relationship $A = \pi r^2$. The 45° cone geometry defines the point when the substrate starts to affect the measured hardness. Thus, $V_s = 0$ for $r < t$, and $V_f = \pi/3\,[r^3 - (r-t)^3]$ and $V_s = \pi/3(r-t)^3$ for $r > t$. By substituting for V_f and V_s into eqn. (5), we obtain

$$H_m = H_f - \chi^3(H_m - H_s)\frac{V_s}{V_f}$$

$$= H_f - \chi^3(H_m - H_s)\left\{\frac{(r-t)^3}{r^3 - (r-t)^3}\right\} \tag{7}$$

Thus, plotting H_m against $(H_m - H_s)V_s/V_f$ should yield a straight line plot with intercept H_f and gradient χ^3.

4. Experimental details

The diamond films were grown at Bristol by hot filament chemical vapour deposition (HFCVD) using a tantalum filament. The growth conditions used a gas mixture of CH_4:H_2, ratio 1:100, with a total flow rate of 200 sccm (standard cubic centimetres min^{-1}) at 30 Torr. The substrates investigated were single-crystal (100) Si and an engineering titanium alloy

(Ti–6%Al–4%V). The silicon substrates were pre-abraded with 1–3 μm diamond powder. The titanium substrates were mechanically polished, finishing with 3 μm diamond paste. No further abrasion was found necessary. During deposition, the temperature at the edge of the substrate was between 700–750 °C; however, it was probably 200 °C higher in the area of deposition. The deposition time was varied from 1 to 6 h, with a growth rate of approximately 0.5 μm $h.^{-1}$ Laser Raman analysis has shown the films grown under these conditions to be diamond, with no graphitic signal.

The film thicknesses were estimated from scanning electron micrographs. These micrographs also show the films' faceted surface morphology. A diamond film on a silicon substrate was tested using a surface roughness machine (Tencor Alpha Step 200). This gave a centre line average roughness (R_a) of 116 nm at a traverse speed of 2 μm $s.^{-1}$ To produce a smoother surface an attempt was made to polish a diamond film mechanically using 1 μm diamond paste on a Kemet iron plate. However, this proved unsuccessful, because part of the film was removed.

The films were indented with a Matsuzawa Seiko microhardness tester, using a Knoop indenter with a dwell time of 15 s. Chipping of the indenter was observed at loads of 50 g, becoming significantly worse at increasing loads. The indent's long diagonal was measured on a Zeiss optical microscope, using Nomarski interference contrast. This was difficult, because the impressions were not sharply defined, owing to the rough surface.

5. Results and discussion

Figures 1 and 2 show hardness results against h/t for diamond films grown on the silicon and titanium alloy substrates. The error bars show 95% confidence limits. The indentation depth is calculated from the long diagonal. For a Knoop indenter, $h = d/\tan(86.25°) \approx d/30$. Figures 1 and 2 also show the results of the linear regression fit of the data to the Bhattacharya and Nix model (eqn. (4)) and to the volume mixtures model (eqn. (7)). Table 1 summarizes the intrinsic hardness predicted from the intercept values for the diamond films on each of the substrates, and gives the coefficient of determination (r^2) for each regression fit.

Since r^2 gives a measure of the variability of the measured hardness which can be attributed to the model, the r^2 values show that the Bhattacharya and Nix model gives the better fit ($r^2 = 0.9537$ means that more than 95% of the variation is predicted by the model). As expected, the results do predict a high hardness for the diamond films, although there are large margins of error in the fits.

The material constants used to calculate the yield stress of the diamond films from the gradient term in eqn. (4) are shown in Table 2, together with the results. Table 3 shows a calculated value for n (eqn. (6)) obtained from the gradient term in eqn. (7).

One source of error is the assumption that the indenter remains perfectly rigid during an indentation, which is

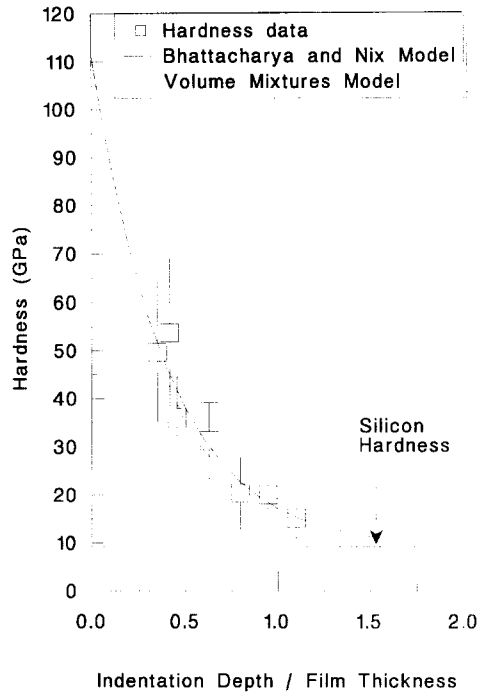

Fig. 1. Hardness data from diamond films on silicon and line fits from the hardness models.

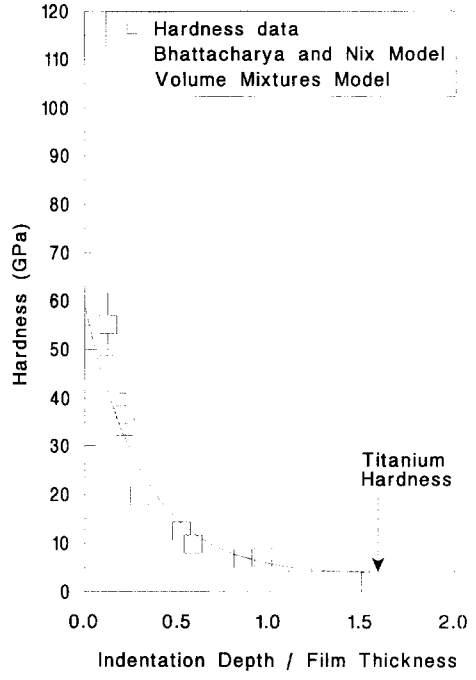

Fig. 2. Data from diamond films on the titanium alloy and line fits from the hardness models.

TABLE 1. Predicted diamond film hardness and coefficient of determination obtained from the hardness models

	Bhattacharya and Nix model	Volume mixtures model
Diamond film on silicon	112 ± 18 GPa $r^2 = 0.9537$	59 ± 12 GPa $r^2 = 0.4629$
Diamond film on titanium	59 ± 18 GPa $r^2 = 0.9293$	38 ± 11 GPa $r^2 = 0.7027$

TABLE 2. Predicted diamond film yield stress from Bhattacharya and Nix model, as well as measured hardness and substrate property data

	Hardness (GPa)	Yield stress (GPa)	Young's modulus (GPa)
Diamond film on silicon	112	7.72	960 [13]
Diamond film on titanium alloy	59	1.71	960 [13]
Silicon	9.0	4.33 [14]	127 [14]
Titanium alloy	3.6	1.00 [15]	110 [15]

TABLE 3. Predicted value of n from the volume mixtures model, with the substrate properties shown in Table 2

	Hardness (GPa)	Young's modulus (GPa)	n
Diamond film on silicon	59	960 [13]	0.124
Diamond film on titanium alloy	38	960 [13]	0.184

unlikely; hence, calculation of the contact area and indentation depth is affected.

Because diamond has a much smaller coefficient of thermal expansion than that of the titanium alloy, a large thermal stress is expected in the diamond film when it is cooled after growth. A diamond film, nominally 4 μm thick, spontaneously debonded after it had been cooled. Microhardness results are affected by the presence of internal stresses.

Another possible source of error is the assumption that a binary layer system is tested. In fact, there is an interface layer of silicon carbide between the diamond film and the silicon substrate, and one of titanium carbide between the diamond film and the titanium substrate. The silicon carbide layer is relatively thin [16] but the titanium carbide layer is much thicker [17], and certainly of an order at which one might expect the microhardness to be affected. Microhardness tests on the titanium alloy sample from which the film spontaneously debonded indicated a 10 g hardness of 8.5 ± 1.1 GPa, which is a large increase on the bulk hardness of the titanium alloy substrate (4.17 ± 0.15 GPa at 10 g).

6. Conclusions

Both models predict a high diamond film hardness, which is further verified by the damage caused to the diamond indenters. The Bhattacharya and Nix model appears to be the more appropriate model ($r^2 > 0.92$), though data at lower h/t ratios are needed to be more certain. However, the difficulties experienced in measuring the indents, the presence of more than one layer and the presence of internal stress lead to errors in the modelling of the films' hardness. Another problem is the high cost of regrinding damaged indenters.

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