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Experimental assessment of the elastic properties of thin TiN/AlN superlattice and nano-multilayer coatings

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Abstract

Nanoindentation is widely used for the mechanical assessment of coatings and thin films. Whereas this can lead to reliable assessments for coating-only properties for short range properties like plasticity the longer range of elastic interactions means that measured data always contains a contribution from the substrate. This paper describes a simple model which can be used to assess the extent of these interactions and predict how changing the elastic properties of individual layers in a complex multilayer or superlattice coating may influence the contact modulus measured by nanoindentation. The model highlights the effect of the transition from hexagonal to cubic AlN as the bilayer period is reduced in TiN/AlN nano-multilayer coatings and how the elastic anisotropy of the layer materials can also be significant in textured coatings.

Keywords

Nanoindentation, coating, elastic properties, Young's Modulus

1. Introduction

Multilayer coatings have been developed for a number of tribological applications because the presence of internal interfaces in the coating promotes high hardness and resistance to fracture [1-5]. Multilayering can also be used to combine the excellent properties of individual materials into a multifunctional stack with superior properties. Multilayer and superlattice coatings based on transition metal nitrides have been very successful in this regard. Superlattice coatings consist of repeated thin layers of two different materials with constant thickness of each layer and a fixed repeat. There are many reports in the literature of the enhanced hardness of such superlattices when the superlattice repeat is reduced to a few nanometres, e.g. for instance it was shown that maximum hardness values for coatings of TiN/VN (~56 GPa), and of TiN/NbN (~51 GPa) could be

produced with good control of the superlattice period that were much higher than the hardness for homogeneous single-crystal coatings of TiN, VN, and NbN (17 to 23 GPa) [6-8]. Many other workers have published work on hardness enhancements in other systems in the intervening years. In most cases genuine superlattice coatings can only be produced by epitaxial growth on substrates with small lattice mismatch and the majority of coatings deposited on engineering substrates can be regarded as nanoscale multilayers of polycrystalline coatings. Despite this enhanced hardness values are still reported [e.g. 9].

There has been much less published on the elastic properties of such multilayer and superlattice coatings with rule of mixtures estimates sufficing to describe the experimental data that has been produced [e.g. 10]. Indeed the mechanisms underlying the hardness enhancements in these systems (inhibition of dislocation motion due to layer coherency strains, increases in total interface area due to glide across the layers, misfit dislocation arrays at the interfaces, the Hall–Petch effect, and image forces due to modulus mismatch between the layers (Kohler effect) [11, 12]) are not expected to have any effect on elastic properties. However, there are some cases where the crystal structure of a material may be changed in a superlattice where this is not the case. An example is the stabilisation of AlN into a cubic form in a TiN/AlN superlattice where the period is restricted to a few nanometres [13]. The cubic form is expected to have a higher elastic modulus than its hexagonal counterpart [14]. However, there are no good experimental measurements which clearly demonstrate that this is the case in TiN/AlN multilayers; the best data shown that the effective shear modulus of a film containing cubic AlN is higher than that of a similar film containing hexagonal AlN [15].

Measurement of the mechanical properties of thin films is not always straightforward. In recent years the most common approach has been to use nanoindentation testing [16]. For coatings less than 1µm in thickness it is often challenging to get a measurement of coating properties independent of the substrate. For instance, the normal analysis method of Oliver and Pharr [17] has been assumed to give a reasonable value for coating hardness if the penetration depth is low enough (typically less than 10% of coating thickness [18]). Whereas there is some validity in this for hardness values the elastic property (contact modulus) data may not be amenable to the same analysis. The ISO14577 standard recommends extrapolating a plot of hardness or contact modulus against contact depth to zero depth to obtain coating properties. Whereas this produces reasonable values for reasonably thick (>1µm) coatings on hard stiff substrates the values determined in this manner for thin films can be greatly underestimated. For indentation tests to give reliable data for any material the scale of the deforming volume must be large compared to the scale of the microstructure otherwise considerable scatter in the data can arise due to crystallographic effects – this is particularly apparent in the elastic properties determined from anisotropic materials such as zinc where grain to grain orientation variations can lead to a factor of three variation in the measured contact modulus [19].

Indentation techniques may be also used to study multilayer coatings [20] but it can be very difficult to obtain the properties of individual layers using the technique. In general, the properties of the outermost layer may be determined if it is thick enough and low enough loads are used in the test but once the deforming volume expands to include material in several layers an averaged behaviour is observed which is related to the indenter penetration and the amount of deformation which

occurs in each layer. In such cases a modelling approach is necessary to determine coating properties. Several methods have been suggested for assessing the plastic contributions of individual layers to the measured hardness [e.g. 21] but work on the elastic response of multilayer coatings is less well developed.

Indeed, it is questionable whether it is possible to determine the elastic properties of a single layer coating independent of the substrate by direct measurement even with an extrapolation approach. The coating and substrate beneath an indenter are effectively two springs in series and thus there will always be a substrate contribution in the contact modulus data measured from them. Thus a modelling approach is necessary to extract the coating properties from the data obtained. A number of workers have developed models based on a weighting the elastic contributions from coating and substrate using either empirical functional forms [22, 23] or more complex analytic expressions [24-26]. The most successful of these use a weight function developed from Gao's model [24, 27] which may be used to predict the variation of elastic properties with contact depth for a single layer coating straightforwardly. However, extending this approach for multilayer coatings is not easy. A simple model has been previously developed for the variation of the contact modulus with contact scale for single and multilayer coatings [28, 29]. In this paper this model has been extended to superlattice coatings and used to determine if the transition from hexagonal to cubic AlN can be reliably detected using nanoindentation data obtained from submicron coatings.

2. The model

Assume that an indenter is loaded onto the surface of the coating with contact radius a_0 . At the surface the load is supported by a contact area $A=\pi a_0^2$ but the area of load support is increased as we consider layers in the coating and substrate below the surface. If we consider the material divided up into a number of layers parallel to the surface then the load on the contact area of the top surface is transferred to a slightly larger area on the next layer below and so-on throughout the coating and substrate thickness. As the area increases the contact stress decreases and, assuming elastic behaviour, the strain in each successive layer is reduced. Thus the displacement of the material due to the loaded indenter is greatest just beneath it and falls away as the distance from the indenter tip increases. Given this observation it should be possible to measure the contribution of the coating to the overall displacement and hence the modulus of the coating if the expression for the change in loaded area with depth is known. Similarly for a multilayer or superlattice coating we should be able to assess the contribution to the overall displacement from the deformation in each individual layer if its elastic properties are known.

Initially consider a single layer coating on a substrate. Let us assume that there is a linear increase in the area supporting the load as we go deeper into that material; this effectively gives us a truncated cone for the loaded volume, seen in cross section in Figure 1a.

If we assume a totally rigid indenter then the indenter displacement, δ , is given by the sum of all the displacements in the individual layers beneath the indenter. In an individual layer

$$d\delta = \frac{Pdx}{EA} \quad (1)$$

Where P is the load applied to the indenter, E is the Young's Modulus of the layer and A is the contact area at a given depth x . If the semi-angle of the cone is α then

$$A = \pi(a_0 + x \tan \alpha)^2 \quad (2)$$

Combining (1) and (2) we have in the coating

$$d\delta = \frac{P}{E_c} \frac{dx}{\pi(a_0 + x \tan \alpha)^2} \quad (3)$$

where E_c is the Young's Modulus of the coating. This can be integrated through the coating thickness to give the total indenter displacement due to elastic deformation of the coating. Thus

$$\delta_c = \frac{P}{\pi E_c} \int_0^{t_c} \frac{dx}{(a_0 + x \tan \alpha)^2} \quad (4)$$

Where t_c is the coating thickness. Integrating gives

$$\delta_c = \frac{P}{\pi E_c} \left[\frac{1}{a_0 \tan \alpha} - \frac{1}{a_0 \tan \alpha + t_c \tan^2 \alpha} \right] \quad (5)$$

By a similar approach integrating through the substrate thickness we have

$$\delta_s = \frac{P}{\pi E_s} \left[\frac{1}{a_0 \tan \alpha + t_c \tan^2 \alpha} - \frac{1}{a_0 \tan \alpha + (t_c + t_s) \tan^2 \alpha} \right] \quad (6)$$

where E_s is the Young's Modulus of the substrate and t_s the substrate thickness. The total indenter displacement is then

$$\delta = \delta_c + \delta_s \quad (7)$$

Both the displacements in the coating and substrate are a linear function of contact load and thus the unloading stiffness $S=P/\delta$. Given that for a flat punch $S=2Ea$ [30] it is possible to calculate the effective Young's Modulus of the coating/substrate system

$$E = \frac{P}{2a_0(\delta_c + \delta_s)} \quad (8)$$

For a deformable indenter E must be replaced by E^* , the contact modulus given by

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \quad (9)$$

Where the subscripts 1 and 2 refer to the properties of the sample and indenter respectively and ν is Poisson's ratio and E is Young's Modulus. For a coated system, E_c and E_s are the contact moduli of coating and substrate respectively. The contact radius can be related to the contact depth, h_c , determined by the Oliver and Pharr method [17], if the indenter geometry is known. For a Berkovich indenter,

$$h_c = \sqrt[3]{\pi/k} a_0 \quad (10)$$

where $k=24.5$. This assumes a perfect tip which is reasonable at larger contact areas corresponding to higher load tests. When comparing with experimental data it should be recognised that the experimental contact depth will have been used to determine a contact area through a measured tip area function – thus for a given contact depth there could be a range of contact moduli depending on the area function; usually lower values are measured for a blunter tip. To avoid this problem the

contact radius can be determined from the contact area, A , determined from the contact depth using the tip area function, via

$$a_0 = \sqrt{A/\pi} \quad (11)$$

Or more conveniently from the load and measured hardness

$$a_0 = \sqrt{\frac{P}{\pi H}} \quad (12)$$

2.1 What is the angle alpha?

Since the indentation of a bulk material is almost identical to that of a coating with large thickness equation (5) can be applied to a bulk material of known elastic properties to determine the truncated cone angle α . If we assume that the material thickness is very much greater than the contact radius the second term in the brackets in equation (5) goes to zero and

$$\delta = \frac{P}{E\pi a_0 \tan \alpha} \quad (13)$$

The unloading stiffness is P/δ and using the Sneddon approximation [30]

$$S = E\pi a_0 \tan \alpha = 2Ea_0 \quad (14)$$

Thus $\tan \alpha = 2/\pi$ and $\alpha = 32.48^\circ$. This angle is independent of the choice of material and the properties of coating or substrate. Combining equations (5), (6) and (8) with this expression for $\tan \alpha$ it can easily be shown that:

$$E = \frac{1}{\frac{1}{E_c} \left[1 - \frac{\pi a_0}{\pi a_0 + 2t_c} \right] + \frac{1}{E_s} \left[\frac{\pi a_0}{\pi a_0 + 2t_c} - \frac{\pi a_0}{\pi a_0 + 2(t_c + t_s)} \right]} \quad (15)$$

From this formulation it is clear that as a_0 tends to zero the value of E tends to E_c and that if a_0 is very much greater than t_c and t_s is much greater than a_0 then E tends to E_s as might be expected. Figure 1b shows a comparison of the predicted variation of contact modulus with contact radius normalised by coating thickness for a single layer coating (Contact modulus 240GPa) on a more compliant substrate (contact modulus 120GPa) using equation 15 and several other predictive models from the literature. Included are the finite element predictions using the same input data which were used to validate the model [29]. Agreement is reasonably good with all the models and the FE data except for the original Gao model implying that the model developed here is at least as good as those previously developed despite its apparent simplicity.

2.2 Multiple Layer Coatings

Equations (5)-(8) can easily be modified for a coating with two or more layers. In the case of a layer on an intermediate layer on the substrate equation (5) remains valid for the coating contribution but, for an interlayer of thickness t_i and modulus E_i , equation (6) becomes

$$\delta_i = \frac{P}{\pi E_i} \left[\frac{1}{a_0 \tan \alpha + t_c \tan^2 \alpha} - \frac{1}{a_0 \tan \alpha + (t_c + t_i) \tan^2 \alpha} \right] \quad (16)$$

And for the substrate

$$\delta_s = \frac{P}{\pi E_s} \left[\frac{1}{a_0 \tan \alpha + (t_c + t_i) \tan^2 \alpha} - \frac{1}{a_0 \tan \alpha + (t_c + t_i + t_s) \tan^2 \alpha} \right] \quad (17)$$

In equations (7) and (8) $\delta_c + \delta_s$ is replaced by $\delta_c + \delta_i + \delta_s$. Thus

$$E = \frac{1}{\frac{1}{E_c} \left[1 - \frac{\pi a_0}{\pi a_0 + 2t_c} \right] + \frac{1}{E_i} \left[\frac{\pi a_0}{\pi a_0 + 2t_c} - \frac{\pi a_0}{\pi a_0 + 2(t_c + t_i)} \right] + \frac{1}{E_s} \left[\frac{\pi a_0}{\pi a_0 + 2(t_c + t_i)} - \frac{\pi a_0}{\pi a_0 + 2(t_c + t_i + t_s)} \right]} \quad (18)$$

The denominator of this equation is the sum of the reciprocals of the elastic moduli of each individual layer multiplied by a geometric factor which depends on the contact radius and individual coating and substrate thicknesses. In fact the thickness contributions in each term represent the distance of the top and bottom of the individual layer from the sample surface.

2.3 Superlattice coatings

Equation (18) can be easily extended to a large number of layers reflecting that the main difference between the geometric factors multiplying the reciprocal moduli are the individual layer thicknesses. In a superlattice every second layer has the same elastic properties and we can collect together the geometric factors for the layers with the same properties. If equation (18) is written as

$$E = \frac{1}{\frac{1}{E_1} geo1 + \frac{1}{E_2} geo2 + \frac{1}{E_s} geosub} \quad (19)$$

where E_1 and E_2 are the contact moduli of the individual layers in the superlattice and the distances of each interface from the surface are t_1, t_2 , etc., it can easily be shown that

$$geo1 = 1 - \frac{\pi a_0}{\pi a_0 + 2t_1} + \frac{\pi a_0}{\pi a_0 + 2t_2} - \frac{\pi a_0}{\pi a_0 + 2t_3} + \dots \quad (20)$$

$$geo2 = \frac{\pi a_0}{\pi a_0 + 2t_1} - \frac{\pi a_0}{\pi a_0 + 2t_2} + \frac{\pi a_0}{\pi a_0 + 2t_3} - \dots \quad (21)$$

$$geosub = \frac{\pi a_0}{\pi a_0 + 2t_c} - \frac{\pi a_0}{\pi a_0 + 2(t_c + t_s)} \quad (22)$$

where t_c is the total superlattice thickness and t_s is the substrate thickness as before. Equations (20) and (21) need to consider all the layers of the same material in the total coating thickness; this can easily be achieved with some simple computation. Equation (19) can then be used to predict the contact modulus of the coating.

2.4 Model Predictions

Predictions of the variation of contact modulus with contact depth are shown in Figures 2 and 3 for idealised TiN/AlN multilayers on a steel substrate (contact modulus $E=200\text{GPa}$). In these Figures the individual layers of TiN and AlN are 20nm thick, the total coating thickness is $3\mu\text{m}$ and the contact modulus of TiN ($E=600\text{GPa}$) is twice that of AlN (300GPa). The main difference between the figures is that the top layer is TiN in Figure 2 and AlN in Figure 3. In each figure the variation of contact modulus with contact depth of single layers of each of the materials and the rule of mixtures average is included for comparison.

In both Figures it can be seen that the predicted superlattice modulus lies between the single layer values as expected and tends to the rule of mixtures value as the contact depth increases. However, at low depths the predicted contact modulus is dominated by the properties of the top layer and rapidly changes in the direction of the rule of mixtures average as the contact depth increases. In both cases here the rule of mixtures overestimates the contact modulus except at very low depths for the TiN top layer. Once the contact depth is greater than the thickness of the top layer its effect can no longer be seen and behaviour representative of the superlattice as a whole is observed.

3. Experimental validation

3.1 Coating/substrate systems investigated

AlN and TiN coatings were deposited onto silicon ($E=175\text{GPa}$) and stainless steel ($E=210\text{GPa}$) by DC magnetron sputtering. The substrate contact modulus values in parentheses were determined from nanoindentation measurements on the uncoated substrate (corrected for pile-up in the case of the stainless steel substrate using AFM images of the impressions created). 99.99% pure titanium and aluminium cathodes were used in a dual cathode opposed configuration. The samples were mounted on a rotating steel prismatic holder between the cathodes so that they alternately faced each cathode at a constant offset distance of 10cm and the holder completely blocked the view of one target from the other to minimise the cross contamination between the cathodes. The system base pressure was 10^{-5} Pa. Argon was initially introduced into the chamber at a working pressure of 0.3Pa and the samples were sputter cleaned by applying a -800V bias to the sample holder. The temperature of the sample holder rose to about 200°C in this process and remained at this level throughout the deposition of the coatings. The bias was then reduced to -100V and 50/50 nitrogen/argon mixture, premixed in a manifold, was introduced into the chamber to allow reactive sputtering and form the nitrides at the samples. The nitrogen partial pressure was controlled by a piezoelectric valve controlled by an optical emission system to ensure target poisoning was minimised and the magnetron power supplied were fitted with arc suppression circuitry. The working pressure was about 0.4Pa throughout the deposition process. The individual layer thicknesses were controlled by the rotation speed of the plate and the power applied to each individual cathode. The deposition rate for the TiN was about twice the deposition rate for AlN at the same applied power so the power applied to the Al cathode was twice the power applied to the titanium cathode to get coatings with equal layer thickness and was increased further to get superlattice coatings with thicker AlN layers compared to TiN layers.

Thick ($>5\mu\text{m}$) single layer AlN and TiN coatings were initially deposited without the sample stage rotation to calibrate the deposition rates and provide samples for characterisation. Both coatings had the expected equilibrium microstructures but were highly textured. X-ray diffraction showed the TiN sample was cubic with the sodium chloride structure as expected and a (200) texture whilst the AlN was the hexagonal Wurtzite structure with a strong (0001) texture. These samples were also used for preliminary nanoindentation trials. The hardness of TiN was 22GPa and AlN was 16GPa and the contact Modulus of TiN was 340GPa and AlN was 235GPa using the ISO 14577 extrapolation method on the data produced. These values are slightly lower than those from samples produced using optimised conditions for a single layer deposited in the system with only a single cathode material used. For hexagonal AlN the Hill average Young's Modulus determined from the single crystal elastic constants in Table 1 is 335GPa giving a contact Modulus of 272GPa with a Poisson's

ratio for the coating of 0.25 which is almost identical to values obtained directly from nanoindentation previously [31]. The value obtained here is a little low compared to what might be expected but is broadly comparable with other reported values from acoustic measurements on bulk material [32]. There is some variation in the literature data for TiN from different sources (labelled as TiN (A) and TiN (B) in Table 1) but the Hill average values for polycrystalline material are around 430GPa giving a contact modulus of 332GPa with a Poisson's ratio of 0.28 which is within experimental error of the measured value. The low value for AlN is probably due to the fact that the samples exhibited columnar growth and were not fully dense but may also be due to the presence of a small amount of amorphous material due to the low deposition temperature. Thin AlN and TiN single layer coatings were then produced for model validation where the coating thickness was 200nm for TiN and 250nm for AlN.

Once the single layer coatings had been characterised a range of nano-multilayer and superlattice coatings were produced with individual layer thicknesses from 1 to 70nm and bilayer periods from 5 to 125nm to a total coating thickness of 500nm. When the period was greater than 10nm the structure of the TiN and AlN layers was cubic and hexagonal as expected from the single layer results although there was some variation in texture in the layers. When the superlattice period was less than 5nm the AlN layers became cubic with the same sodium chloride structure as TiN. Representative samples from above and below this transition were then selected for detailed mechanical analysis.

3.2 Nanoindentation testing

Coated samples were attached to a heavy steel block using cyanoacrylate adhesive prior to testing to minimise support compliance issues. Nanoindentation testing was performed on a Hysitron Triboindenter fitted with a used Berkovich diamond (average tip end radius 120nm determined from elastic indentations in fused silica). Indentation tests were performed under displacement control with a loading and withdrawal rate of 500nm/s and a 4s peak load hold to allow for creep run out. A 40s 2 μ N contact load hold prior to the test was used for thermal drift correction. Hardness and contact modulus data were determined from the load displacement curve by the method of Oliver and Pharr [17]. Tip end-shape calibration was performed using a fused silica standard prior to testing using the Oliver and Pharr approach. Indentations were produced at a range of peak displacements from 3 to 400nm depending on the sample.

3.3 Modelling of single crystal elastic constants

The second order elastic constants of the three Al nitrides, Wurtzite, zinc blende and rock salt have been determined from ab initio calculations using the generalized gradient approximation. The space groups corresponding to the crystal structures considered were *P63mc* (186) for Wurtzite, *F-43m* (216) for zinc blende and *Fm-3m* (225) for rock salt. The ab initio calculations were carried out with the Quantum-ESPRESSO package [33] using atomic ultrasoft pseudopotentials [34]. The *k*-points meshes were constructed according to the Monkhorst-Pack scheme [35] and the Brillouin zone integrations were performed according to the Marzari-Vanderbilt method [36]. A mesh 11x11x7 was selected for the hexagonal structure and 8x8x8 for the cubic structures. A plane wave kinetic energy cutoff of 75Ry and a charge density cutoff of 600Ry were sufficient to achieve convergence for all three structures. Each structure was then optimised by computing the total energy as a function of the unit cell volume.

The elastic constants were calculated using the ElAStic code [37] by applying small Lagrangian strains (-0.001, -0.0005, +0.00001, +0.0005 and +0.001) to the optimised unit cells and computing the total energy.

4. Results

In the case where the properties of the coating and substrate are well known equation (15) can be used to predict the elastic response of the coating/substrate system where for the superlattice layers equation (19) has been used in the following comparisons with experimental data. The following subsections consider different types of coating/substrate system.

4.1 Monolayer Coatings

Figure 4 shows a comparison between the predicted variation of contact modulus with contact depth for 250nm AlN on silicon compared to experimental data. The model parameters were taken from a much thicker coating. Good agreement between model and experiment is observed at the greater depths but the experimental data diverges from the model at the lowest depths. This is because the Berkovich tip used is not perfectly sharp and the blunt end initially cannot create any plastic deformation so the Oliver and Pharr analysis is invalid. Once the elastic-plastic transition occurs there is a rapid increase in contact modulus until the model and experiment agree. In these circumstances the plastic zone beneath the indenter is fully developed and the Oliver and Pharr analysis is valid.

It is often suggested that a plateau in the measured data at low loads gives a representative value for the coating hardness or contact modulus. This is clearly not the case here. It is also suggested that low penetration data may be extrapolated to zero depth to give the coating properties in the ISO14577 standard but it is clear that the data obtained during the elastic-plastic transition must be removed if this is to be accurate. Furthermore, for thin coatings such as this the extrapolation process will underestimate the coating properties because insufficient good data for extrapolation is available at low contact depths.

Similar conclusions can be drawn from the data for 200nm TiN on silicon in Figure 5. The agreement between model and experiment is reasonable though there are some deviations below a contact depth of 100nm which implied that the elastic properties of the coating do not vary significantly with thickness as might be expected. This is the regime where the tip blunting is most significant and the accuracy of the conversion from contact radius to contact depth is questionable. The extrapolation of the experimental data to zero contact depth following ISO14577 will again underestimate the contact modulus of the coating.

4.2 Nano-multilayer coatings with large period

Figure 6 shows a comparison between predicted and experimental contact modulus as a function of contact depth for a 500nm thick TiN/AlN nano-multilayer on silicon with a period of 125nm. Each material has a layer thickness of 62.5nm in this case. For this sample X-ray diffraction shows that the AlN retains the hexagonal Wurtzite structure of the single layer coating and the hexagonal AlN properties were used in the model prediction. The fit between experiment and model is excellent.

The rule of mixtures average contact modulus is shown for comparison and is almost identical to the superlattice model except at low contact depths where it underestimates the contact modulus. The experimental data again shows an elastic-plastic transition but once this is complete the agreement with the model is maintained across the contact size range.

The hardness of this coating is about 33GPa which is higher than either of the individual layer hardnesses showing the benefits of the multilayering approach.

4.3 *Nano-multilayer coatings with small period*

Superlattice coatings were produced with much thinner layer periods to determine the effect of cubic AlN on the measured properties. The most successful coating deposited was based on a 1nmTiN/4nmAlN superlattice with a total thickness of 500nm deposited on steel. This sample showed a good epitaxial match between the cubic TiN and cubic AlN and a hardness of about 48GPa. This high hardness means that the elastic-plastic transition behaviour occurs at greater depths and there are relatively few good values for contact modulus that can be compared with model predictions. Thus a large number of indentations were performed at a small number of specified contact depths to determine the data in Figure 7.

To make predictions the contact moduli obtained using thicker layers of TiN and AlN were initially used but the agreement with experimental data was poor. This is due to the fact that these multilayer coatings contain the cubic material which has a higher contact modulus (Table 1). There is some variation in the elastic constants obtained from different literature sources so theoretical calculations have been run to determine suitable values to use for modelling in this study. AlN can have two cubic forms the B3 zinc blende structure and the rock salt B1 structure – the latter structure produces a stiffer material (Table 1) and is more likely to form in templated growth on TiN which has the same crystal structure. This was observed by X-ray diffraction on the samples tested in this study.

Predictions were the run fixing the properties of cubic TiN (contact modulus 415GPa) and cubic AlN (rock salt structure contact modulus $E=364$ GPa) and hexagonal AlN (contact modulus 250GPa) for comparison with the experimental data in Figure 7. These values were chosen as about the maximum elastic properties which might be expected based on the literature data and the experiments on thicker coatings. The rock salt cubic structure prediction clearly matches the experiment rather than the hexagonal data used previously as expected from the structural analysis of the coatings.

Both cubic forms of AlN are very anisotropic and have a much higher stiffness in [111] compared to [100] whereas for TiN the [100] stiffness is higher (Table 2). Since the deposited coatings showed a considerable texture it might be that the differences observed are related to crystallographic orientation rather than phase composition when it is considered that it is the elastic displacements in the direction of loading which dominate behaviour in the indentation test. The predictions in Figure 8 have been made assuming (111) and (200) texture B1 cubic coatings have been produced. The experimental data is closer to the (111) prediction which fits with the predominant texture observed for these coatings by X-ray diffraction.

5. Discussion

The use of nanoindentation testing to determine accurate values for the contact modulus of the coating in a coated system is more difficult than for hardness since the elastic response is a long range effect and there is always a contribution from the elastic modulus of the substrate in the measured data. The ISO14577 part 4 extrapolation method suggests that extrapolation of the measured contact modulus data to zero contact depth to determine the properties of the coating. Whereas this approach works reasonably well for thick stiff coatings on stiff substrates insufficient low load data is obtained for thinner films to get a reliable fit and the contact modulus by extrapolation tends to underestimate the real value.

This is particularly true in cases where tip bluntness, and hence the elastic-plastic transition, affects the measured data. In the case of very hard coatings it can be impossible for plastic deformation to occur at the critical depths where data is needed for a high quality extrapolation. Work by Korsunsky and Constantinescu [38] has shown that the contact modulus of a coated system measured by indentation does not converge to the coating value at low penetration unless the radius of the indenter is less than 10% of the coating thickness. Despite the fact that a relatively sharp Berkovich indenter was used in this work this criterion has not been met since the ratio of tip radius to coating thickness is ~ 0.3 for the superlattice coatings. In addition, the data obtained at low penetration depths is significantly affected by tip calibration issues and many indentations do not show plastic deformation so there is a lack of data to use in the fit. This indicates that a curve fitting approach will not produce reliable coating data for very thin stiff coatings on more compliant substrates. With most practical indenters a coating thickness of at least $3\mu\text{m}$ is required to ensure that a good value for coating modulus can be extracted.

Using the modelling approach developed here it has been possible to show that the formation of B1 cubic AlN produces a stiffer superlattice coating and that the properties of the cubic AlN are similar to those from theoretical calculations. However, the fact that the elastic properties of an individual layer will also depend on its microstructure (porosity and texture) must be taken into consideration if the elastic response of the coating is to be fully understood.

6. Conclusions

In this paper we have developed a model to predict the variation of contact modulus with contact radius (and by extension contact depth) for a superlattice coating system. Since elasticity is a long range property there is nearly always a contribution from the substrate in any experimental measurement and the model can help to understand the extent of this effect. In coating development projects a large number of different coatings are deposited with different conditions onto convenient substrates such as silicon. Usually the thickness of these coatings is much less than one micron because the deposition is quick and convenient and the thickness is large enough for chemical analysis. Although it is possible to obtain reasonable hardness values from such films it is very difficult to obtain reliable contact modulus values, particularly if the coating is very hard. The model can help to understand the observed behaviour – in this study we have identified the effect of the transition from hexagonal to cubic AlN on the measured contact moduli of AlN/TiN superlattice coatings. However, if accurate values of contact modulus for coatings are to be measured thicker coatings must be deposited, typically greater than $3\mu\text{m}$ for hard coatings on a stiff substrate.

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Tables

Table 1: Single crystal elastic constants for TiN and AlN. The Voigt, Reuss and Hill average values for polycrystalline materials were calculated by the method outlined in [42].

Material	Elastic Constants (GPa)									Reference
	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	Voigt	Reuss	Hill Average	
TiN (A)	625	165			163		475	395	435	[39]
TiN (B)	575	130			163		458	358	423	[40]
Cubic AlN (B3 - Zinc Blende)	304	160			193		352	300	326	[41]
Zinc Blende AlN	280.2	148.8			218.7		371.3	284.0	329.0	This study
Cubic AlN (B1 - Rock salt)	418	169			308		537	481	509	[40]
Rock salt AlN	443.2	184.3			303		544.1	476.0	510.7	This study
Hexagonal AlN - Wurtzite	411	149	99	389	125	131	340	329	335	[41]
Wurtzite AlN	409.6	108.2	74	400.6	117.2	150.7	340.4	334.0	337.3	This study
Silicon	166	64			79		166	141	153	[14]

Table 2: Young's Modulus in given crystallographic directions for cubic nitrides

Material	E ₁₁₁ (GPa)	E ₁₁₀ (GPa)	E ₁₀₀ (GPa)	Single crystal data from
TiN (A)	418	445	556	[39]
TiN (B)	409	433	527	[40]
AlN (Zinc Blende)	442	335	194	[41]
AlN (Zinc Blende)	475	335	177	This study
AlN (Rock salt)	656	520	321	[40]
AlN (Rock salt)	661	532	335	This study
Silicon	187	169	130	[14]

Figures

Figure 1: (a) Cross sectional view of model geometry and (b) model validation by comparison with other literature models and FE analysis with the same input data.

Figure 2: Model predictions for an idealised 20nmTiN/20nmAlN nano-multilayer of 3 μ m thickness on steel where $E_{\text{TiN}}=2E_{\text{AlN}}$ and TiN is the top layer.

Figure 3: Model predictions for an idealised 20nmAlN/20nmTiN nano-multilayer of 3 μ m thickness on steel where $E_{\text{TiN}}=2E_{\text{AlN}}$ and AlN is the top layer.

Figure 4: Model predictions compared to experimental data for a 250nm AlN coating on silicon. The model was parameterised using modulus data from a thicker (>3 μ m thick) coating (Contact Moduli AlN =235GPa, Silicon=170GPa).

Figure 5: Model predictions compared to experimental data for a 200nm TiN coating on silicon. The model was parameterised using modulus data from a thicker (>3 μ m thick) coating (Contact Moduli TiN =340GPa, Silicon=170GPa).

Figure 6: Predicted vs experimental contact modulus as a function of contact depth for an equal layer thickness TiN/AlN superlattice coating on silicon with period 125nm (total thickness 500nm) using the single layer properties in Figures 4 and 5.

Figure 7: Predicted contact modulus with contact depth for a 1nmTiN/4nm AlN superlattice with 500nm total thickness on steel compared to experimental data. The fit is better when the properties of cubic AlN are used.

Figure 8: Predicted contact modulus with contact depth as a function of crystallographic orientation for a 1nmTiN/4nm AlN superlattice with 500nm total thickness on steel compared to experimental data. The fit is better for the (111) texture.

(a)

(b)

Figure 1: (a) Cross sectional view of model geometry and (b) model validation by comparison with other literature models and FE analysis with the same input data.

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