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Nano-scratch testing of (Ti,Fe)N_x thin films on silicon

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ABSTRACT

Thin films of (Ti,Fe)N_x have been produced on silicon wafers with a wide range of compositions and mechanical properties to investigate correlations between the mechanical properties measured by indentation and crack resistance in the highly loaded sliding contact in a nano-scratch test. The nano-scratch test data on the thin films using a well-worn Berkovich indenter with ~1 μm end radius were supported by high resolution scanning electron microscopic (SEM) imaging and analytical stress modelling. The results show that mechanical properties of the coating, its thickness and the substrate properties all influence the deformation process. They affect the critical loads required, the type of failures observed and their location relative to the moving probe. The differences in coating mechanical properties affect how the interface is weakened (i.e. by initial substrate or coating yielding or both) and determine the deformation failure mechanism. The load dependence of the friction coefficient provides details of the sliding contact zone and the location of failure relative to the sliding probe. Improved performance was achieved at intermediate hardness and H^3/E^2 in the nano-scratch tests on thin films. The friction and modelling results strongly suggest that failure at low load on the hardest coatings is due to a combination of high tensile stress at the rear of the contact zone and substrate yield. Designing thin films for protective coatings with in-built dissipative structures (such as soft and low elastic modulus inclusions) and mechanisms to combat stress may be a more successful route to optimise their toughness in highly loaded sliding conditions than aiming to minimise plasticity by increasing their hardness.

1. Introduction

The successful use of ceramic thin films as protective coatings in demanding applications heavily relies on understanding their properties and the ability to predict their behaviour based on other more easily measured properties. With the popularity of Archard's law, hardness has long been considered the most important property for wear resistant materials. However, it has gradually been realised that other parameters combining hardness (H) and elastic modulus (E), such as H/E and H^3/E^2 may be equally important predictors of wear in many practical applications. In dry sliding and abrasive contact wear resistance has been found to correlate more closely with H/E than with hardness alone [1–2]. The dimensionless ratio H/E is a measure of the elastic strain to break and is strongly correlated with energy dissipation in mechanical contact and can easily be obtained in a nanoindentation test from H/E_r (where E_r is the reduced indentation modulus) [3–7]. In a nanoindentation test the parameter H/E_r is correlated (i) with the indentation plasticity index which is the plastic or irreversible work done during indentation (W_p) divided by the total elastic (W_e) and plastic work done during the indentation and (ii) with h_r/h_{max} where h_r = residual indentation depth and h_{max} = maximum indentation depth with the relationship taking the form

$$\textit{Plasticity index} = W_p/(W_p + W_e) \approx h_r/h_{max} \approx 1 - x(H/E_r) \quad (1)$$

The reduced indentation modulus E_r appears in Eq. (1) rather than the elastic modulus since the shape of the indentation curve is subtly influenced by the stiffness of the indenter, so that lower plasticity indices and greater elastic recovery are observed with lower modulus cBN and sapphire indenters than with diamond [8]. H^3/E^2 is a measure of the resistance to plastic deformation. According to the contact mechanics analysis developed by Johnson, the critical load for the onset of plastic flow should scale with H^3/E^2 in the spherical indentation of bulk materials [9] so for a given applied load contact is more likely to be elastic if H^3/E^2 is increased.

Increasing hardness is often associated with a reduction in toughness, and high hardness alone is no guarantee of high wear resistance in highly loaded mechanical or tribological contact applications where toughness and damage tolerance can be more critical. Ceramic thin-film research has moved away from focusing solely on hardness towards developing hard-yet-tough or super-tough coatings that are designed to be crack resistant and damage tolerant under severe contact conditions [10–23]. Toughening strategies include ductile phase

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toughening (for example by addition of metallic phases such as Al to hard amorphous carbon films, or Ni to nc-MeN/a-SiN_x), compressive stress toughening, mechanical property optimization combined with optimization of the coating architecture by developing coatings with dense non-columnar microstructures, gradient structures with no stress discontinuities from sharp interfaces or multilayered structures with a high number of interfaces for crack deflection. In highly loaded contact applications, coatings with higher plasticity in indentation (i.e. lower H/E) can show higher durability [6,24], although in other studies lower plasticity (i.e. higher H/E) and high H^3/E^2 have also been shown to be beneficial [25–27]. In the design of multilayer coatings for erosion protection Klemberg-Sapieha and co-workers have shown that increasing H^3/E^2 can be highly desirable [26–27]. A coating with high H^3/E^2 and lower elastic modulus than the substrate can spread the load over a larger volume. This can delay the onset of plastic deformation in the substrate and subsequent cracking and chipping of the coating due to the development of tensile stresses on the coating side close to the substrate-coating interface that result in cracks.

In this study the durability of TiFeN coatings on silicon to highly loaded sliding contact has been assessed using the nano-scratch test. The scratch test was initially thought of as primarily an adhesion test, with higher critical loads directly corresponding to more adherent films, but there is now a substantive body of evidence showing that it is the mechanical properties of the film and substrate that exert a significant influence on the deformation behaviour rather than the adhesion strength alone [28–38]. The critical load is dependent on many factors in addition to the interfacial strength. As noted in ASTM C1624 [38] the test method does not measure the fundamental "adhesion strength" of the bond between the coating and the substrate. Instead it "provides a quantitative engineering measurement of the practical (extrinsic) adhesion strength and damage resistance of the coating-substrate system as a function of applied normal force" [38]. One problem with the conventional (macro-scale) scratch test is that the probe radius (200 μm) is very large in comparison to the thickness of the coatings. The maximum von Mises stresses are typically far into the substrate at the critical load and substrate yield occurs before the coatings fail [39]. In a recent study, Wang and co-workers reported that the critical load for coating failure on a range of DLC and TiN coatings on titanium alloys did not depend on coating composition, but correlated directly with the hardness of the substrate [40]. The significance of substrate yield was emphasized by cross-sectional profiles of the scratch depth at failure which were much larger than the coating thickness.

The sensitivity of the scratch test to coating and interfacial properties can be increased by decreasing the probe radius and performing nano-scratch tests. We have previously reported that a-C [41], TiFeN [7] and nc-TiN/a-SiN_x [32] films deposited on silicon with high hardness can perform poorly in nano-scratch tests showing significant delamination extending far from the scratch track. However, in these previous studies it was not possible to fully determine the relationship between mechanical properties and scratch behaviour due to the limited number of samples tested. In this study a larger set of 18 TiFeN coatings were deposited on silicon by PVD with and without ion beam assistance (IBAD), with additional TiN and FeN films deposited for comparison. Although deposition rates are slower than in commercial PVD and CVD coating processes, the dual ion beam approach provides the flexibility and control of nitrogen content in the deposited films to obtain a wide range of mechanical properties. With this larger sample set it has proved possible, supported by high resolution SEM imaging, to investigate the relationship between mechanical properties and the scratch test critical load and deformation over a wide range of coating hardness and H^3/E^2. The variation in friction with increasing load has been investigated to understand the real contact area in sliding with the frictional response at failure providing the location of failure relative to the sliding probe. Analytical modelling of the main stresses was able to suggest how differences in coating mechanical properties affect the initial interface weakening (i.e. by initial substrate or coating yielding or both) and determine the deformation failure mechanism.

2. Experimental

2.1. Film deposition

A sample set of 18 $(Ti,Fe)N_x$ films were deposited on pre-cleaned mirror polished Si (100) wafer substrates using a dual ion beam sputtering system described in detail previously [42]. Sputtering of the target was by a 1.25 keV Ar^+ ion beam with a 280–600 eV N_2^+ ion beam also used for ion-assistance of the deposited film in some cases. The sputter target comprised Ti and Fe with the area occupied by the Fe determining the relative Ti-Fe ratio in the coating. A thin Ti layer was initially deposited onto the Si surface to improve adhesion and the hard coating then deposited onto this bonding layer. Nitrogen ions from the second source bombarded the growing coating during ion-assisted nitride sputtering which occurred in a nitrogen partial pressure of $1–2 \times 10^{-2}$ Pa. The substrate temperature was in the region 85–100 °C. Where films failed by delamination in the nano-scratch test it was possible to determine the film thickness and compare this with the thickness determined from SEM analysis of film cross-sections. Including the thin titanium interlayer the films were typically around 1.3 μm thick, with all being in the range 1.0–1.7 μm. For comparison FeN and TiN films were also deposited on silicon under similar conditions (the same thin Ti interlayer and similar overall film thickness).

2.2. Film characterisation

Nanoindentation and nano-scratch testing was performed using the Micro Materials NanoTest system. Multi-cycle load-controlled "load-partial-unload" experiments were performed up to 20 mN maximum load to assess the variation in mechanical properties with penetration depth. The unloading curves were analysed using standard methods with the area function for the Berkovich diamond indenter determined by indentations into fused silica. Film-only hardness was determined from the plateau (load-invariant) region and film-only elastic modulus by extrapolation to zero depth (following the extrapolation procedure outlined in ISO 14577-4 [43]). The reduced indentation modulus (E_r) can be converted to the Elastic modulus of the material according to Eq. (2).

$$\frac{1}{E_r} = \frac{1-v_s^2}{E_s} + \frac{1-v_i^2}{E_i} \tag{2}$$

where E_s and E_i are the elastic moduli of the sample and indenter and v_s and v_i are the Poisson's ratios of the sample indenter respectively. In this paper E measurements are reported, after conversion of E_r to E using a Poisson ratio of 0.22. The H/E values of the TiFeN films are typically ~20% higher than their corresponding H/E_r values.

For the nano-scratch tests a well-used Berkovich indenter (end radius ~ 1000 nm) was used scratching edge-forward. An indenter was chosen with an end radius sufficiently rounded to avoid the possibility of indenter wear during the highly loaded scratches on the hard films. No evidence for indenter wear was found, as confirmed by subsequent re-testing showing the critical loads were unchanged. The NanoTest has high lateral stiffness minimising any influence of surface roughness so that scratch tracks remain smooth until film failure. The nano-scratch test involved three scans at 10 μm/s over a 600 μm track. In the initial (pre) and final (post) scans the applied load was 0.1 mN. In the second (progressive load scratch) scan the load was 0.1 mN for the first 0–100 μm and then linearly ramped at 10 mN/s to 500 mN. 5 repeat 3-scan scratch tests were done on each sample, with adjacent tracks separated by 50 μm. The first pre-scan at the 0.1 mN contact load was used to measure the film roughness. All the films had a low R_a roughness of 2–4 nm when measured over 100 μm. A Zeiss