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Mechanical Stability and Decohesion of Sol-Fel Hybrid Coatings on Metallic Substrates

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ABSTRACT

The mechanical properties and adhesion behaviour of coatings based on organically modified silanes and synthesized using sol-gel technology were assessed using nano-indentation and microtensile testing, respectively. The relationship between the film structure and its mechanical response is examined. It is shown that the mechanical properties (hardness and Young's modulus) of the coatings is influenced dramatically by the organic substituent and the presence of an oxide layer thermally grown on the substrate material prior to deposition plays an important role on the film/substrate adhesion behaviour.

Keywords: Sol-gel, cracking, debonding, adhesion.

1 INTRODUCTION

The adhesion and mechanical stability of thin film coatings on substrates is increasingly becoming a key issue in device reliability as technology driven products demand smaller, thinner and more complex functional coatings. It is well known that the reliability of metallurgical protective coatings and microelectronic circuits containing multilayered thin film structures is strongly influenced by their interfacial properties, namely strength, fracture resistance and adhesion. Hence, characterizing and understanding the cracking evolution, debonding behavior and adhesion performance of thin films subject to external applied stresses is crucial when planning such applications. By using micro-mechanical in-situ tensile experiments it is possible to detect and analyze the critical conditions for cracking and debonding of the thin film [1, 2]. These types of experiments have been shown to offer new insights into evaluating mechanical response of thin coatings and multilayered structures [1, 3, 4] which has direct relevance to damage evolution and interfacial adhesion.

Sol-gel hybrid coatings, also known as "ormosils" (organically modified silicates), up to several hundred nanometers thick are used to modify the functional behavior of the inorganic component for plastic and metal surfaces to confer wear/abrasion resistance and corrosion protection, respectively [5,6] The unique advantage of hybrid coatings is the combination of properties obtained from the organic and inorganic constituents. It has been shown that the mechanical properties are highly dependent on the composition and chemistry of the organic species [7, 8]. Despite this, the film cracking and adhesion performance of these hybrid thin films when subjected to externally applied stresses remains an essential aspect to investigate, to establish the mechanical stability/reliability of the coated system before use in service.

Characterization of the film cracking and debonding is achieved primarily by in-situ optical microscopy and subsequent scanning electron microscopy (SEM). Load-partial unload data from nano-indentation of the coatings on copper were used to determine the film properties and to provide data for future fracture and adhesion analyses. Implications concerning the influence of the thermal oxide layer on the interfacial adhesion behavior of the sol-gel coatings are discussed.

2 EXPERIMENTAL

Sol-gel coating solutions were prepared by adding a 0.01 M solution of HNO_3 to a mixture of the inorganic constituent tetraethylorthosilicate (TEOS) and the organic constituent glycidoxypropyltrimethoxysilane (GTMS) in ethanol. The solutions prepared were: (i) 100% TEOS (designated TS) and (ii) an equimolar mixture of TEOS and GTMS (designated GT). Each solution contained an equivalent SiO_2 concentration of 5 wt% and a water-to-alkoxide mole ratio of 10. The solutions were spin coated (5000 rpm, 120 s) on 1 µm polished tensile coupons of Cu, Al and Ti (length, 33 mm; width, 3 mm; thickness, 1–1.80 mm; and gauge length, 11 mm) and then dried at 60°C for 24 h. Further details of the sol-gel process are given elsewhere [9]. Prior to spin coating several coupons were heated to 200°C for 3 h to grow the oxide layer.

All films were transparent and the average thicknesses of the dried films, determined using ellipsometry (Rudolph AutoEL) yielded 186 nm for the TS film and 402 nm for the GT films. The thicknesses of the thermal oxide layers were estimated by diffusion theory assuming a parabolic rate law for oxidation [10]: $z^2 = 2K_pt$ where z is the thickness, t is the time and K_p is the rate constant for oxidation [11]. For Cu the oxide thickness was calculated to be $z \approx 125$ nm, for Al $z \approx 130$ nm and for Ti $z \approx 25$ nm.

Mechanical characterisation of the coatings was carried out using a depth-sensing nano-indentation tester with a sharp Berkovich (three-sided pyramidal) diamond indenter and a 1 µm radius tipped spherical diamond indenter. Measurements of the indentation response of the TS and GT coatings on the as-received copper were made using: (i) continuous load-displacement with the Berkovich indenter and (ii) load partial-unload with the spherical indenter. Indentations in both modes were performed with peak contact loads, P, of 0.2, 0.5 and 1 mN, with a minimum of three indents for each load. The load-partial unload data were analysed with the method of Field and Swain [12, 13], from which the contact pressure (hardness) and effective Young's modulus were obtained as a function of penetration depth.

The adhesion behaviour of the coatings was ascertained by simple tensile pulling tests using a specially designed mechanical testing device [1]. The applied load and displacement were recorded during the experiments so that the strains at which film cracking and debonding occurred could be determined. After testing, higher magnification views were obtained on carbon coated samples using scanning electron microscopy (SEM, JEOL 6300).

3 RESULTS AND DISCUSSION

The indentation load-displacement curves are shown for the TS and GT coatings deposited on copper substrates for one continuous loading cycle in Figure 1. For the TS film, the load-displacement curve is typical of an elastic-brittle material. By contrast, the GT film displays a rather unique load-displacement response far removed from the typical elastic-brittle response observed for the TS film. This load-displacement response is characteristic of bulk polymers and rubbers, which display viscoelastic behavior.

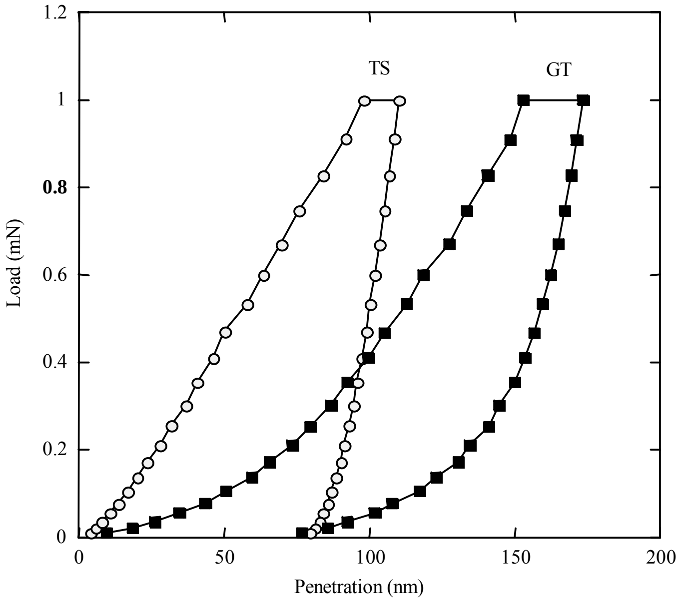


Figure 1: Indentation load-displacement curves for the TS and GT coatings on as-received copper using Berkovich indenter.

The hardness, H, and Young's modulus, E, of the TS and GT films as a function of normalized contact radius, a/t, (where t is the film thickness) were determined using the load-partial unload technique [14]. For TS a value of H = 2.4 GPa and E = 43 GPa were obtained. For the GT film the evaluation yielded H = 0.41 GPa and E = 1.7 GPa. There is evidence of a transition from elastic-brittle to a viscoelastic behavior in the sol-gel material solely due to the influence of organic species and its modifying ability on the inorganic network structure [9, 14].

The critical strains that first cracking of the film, σ_c, and debonding, γ_i, of the film from the underlying substrate were observed in the tensile tests are presented in Table 1. Also given in the table are the calculated fracture parameters, namely the critical stress for cracking ($\sigma_c = \varepsilon_c E_f$), the film toughness ($K_{IC}$) and the interfacial fracture energy (γ). The film toughness is given by [1]:

$$K_{IC} = \left(\sigma_c^2 t \left[\pi F(\alpha_D) + \frac{\sigma_c}{\sqrt{3}\sigma_Y} \right] \right)^{1/2} \quad (1)$$

And interfacial fracture energy by:

$$\gamma_i = \frac{1}{2} E_f t \varepsilon_i^2 \quad (2)$$

Where t is the film thickness, E_f is the film modulus, F is a function of the elastic contrast. It is immediately apparent from the calculated properties that the GT coated as-received aluminum yields the highest toughness film and interfacial adhesion. The film damage observations presented below tend to confirm these results.

Table 1: Fracture parameters from tensile testing of GT coated metal substrates.

Substrate	Critical strain for film cracking (%)	Critical cracking stress (MPa)	Film fracture toughness (MPa.m$^{1/2}$)
Cu	2.3	38	0.037
Cu + thermal oxide layer	4.0	68	0.068
Al	5.8	98	0.096
Al + termal oxide layer	3.4	58	0.055
Ti	3.7	63	0.061
Ti + thermal oxide layer	2.7	46	0.044

Substrate	Critical strain for film debonding (%)	Interfacial fracture energy (J/m^2)
Cu	13.7	6.4
Cu + thermal oxide layer	14.2	6.9
Al	18.4	11.6
Al + termal oxide layer	12.2	5.1
Ti	6.2	1.3
Ti + thermal oxide layer	15.9	8.6

The micrograph of the film cracking behavior of the baseline TS coating on the as-received copper is shown in Figure 2. The damage pattern is similar to that observed on the same coating deposited on stainless steel [9]. There is an extensive array of regularly spaced parallel cracks, sometimes referred to as transverse cracks (loading direction is vertical) which predominate in the coating and throughout the entire gauge length of the specimen. The intercracking distance is quite uniform ≈ 4 µm. This intercrack spacing reduces in extent during stressing to a point of crack saturation as in the present case beyond which no further cracking of film is possible. Also apparent in the micrograph are lighter contrast regions of the film that are associated with delamination from the substrate surface. These debonded zones vary somewhat in size and the film has fractured through or at the edges of the buckled film. The tests have been made at a common imposed total strain of ≈15%.

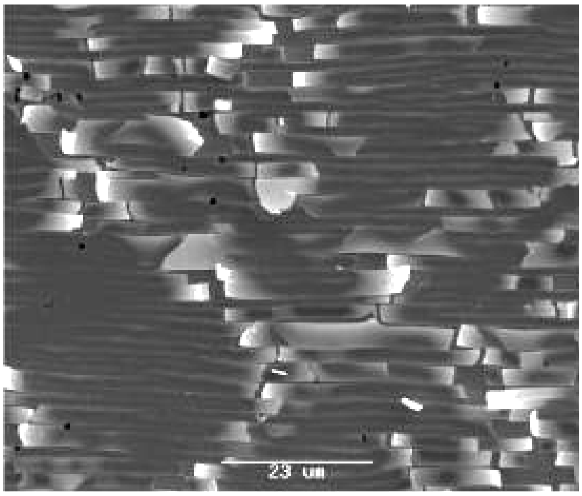
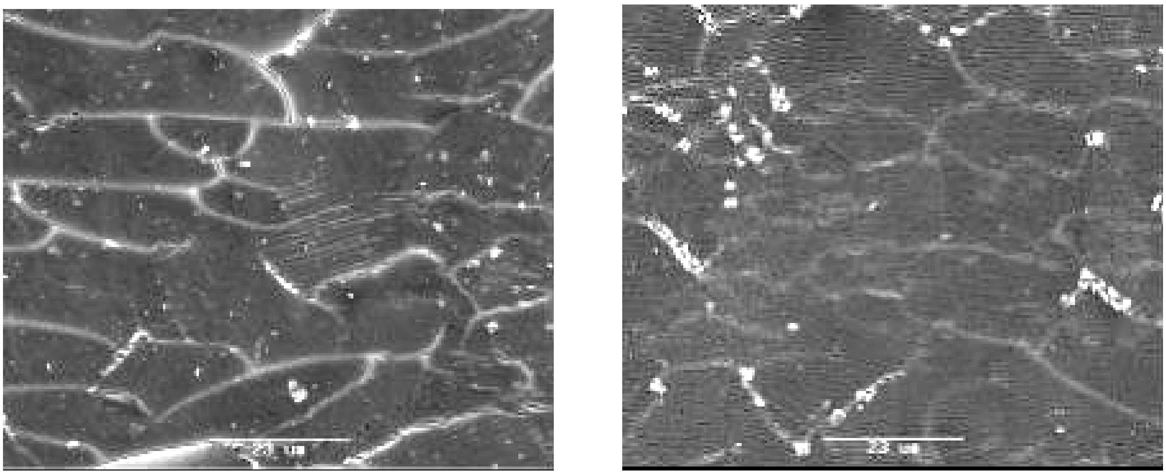


Figure 2: SEM micrograph of cracking and debonding in the TS coating after tensile testing (15% tensile strain). The direction of the applied tensile stress is in the vertical direction.

Copper Substrate: In the GT film on the as-received copper Figure 3a, the observed irregular crack geometry is generally quite characteristic of the GTMS modified coatings on metal substrates [9, 14]. In the corresponding film on the thermally oxidised copper , the coating damage is strongly modified by the thermal oxide interlayer. There is extensive transverse cracking apparent contained within the thermal oxide layer and some small, mainly parallel cracks that traverse the thermal oxide and GT layers. This microstructural features are shown in Figure 3b.

Aluminium Substrate: For the GT film on the as-received aluminium substrate, the irregular cracking is again confined to the coating and there are very few debonded areas. For the thermally oxidised aluminium the prevailing features are large open cracks extending through the coating and oxide layer. Higher-magnification examinations Figure 4, show that small transverse cracks within the oxide layer are evident and there is considerable debonding and buckling of the GT film.



a) **b)**

Figure3: SEM micrographs of cracking and debonding in the GT coating on copper after tensile testing (15% tensile strain): (a) as-received copper and (b) thermally oxidised copper. The direction of the applied tensile stress is in the vertical direction.

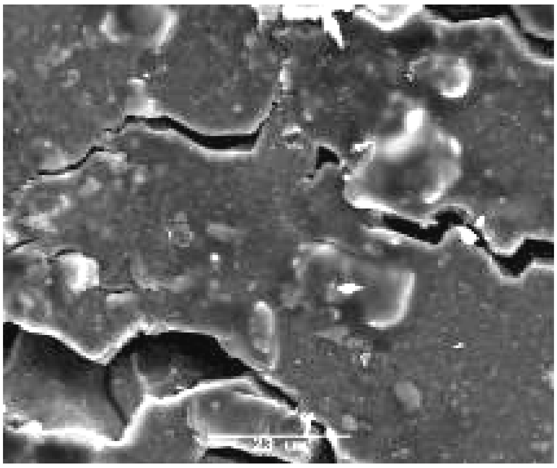


Figure4: SEM micrographs of cracking and debonding in the GT coating on thermally oxidised aluminium after tensile testing (15% tensile strain). The direction of the applied tensile stress is in the vertical direction.

Titanium Substrate: In the GT coating on the as-received titanium substrate the cracking damage pattern is equivalent to that of the as-received copper but the density of cracking is less. Delamination is not extensive but the size of the debonded film is large in size (80-100 µm). For the GT coating on the thermally oxidised titanium the fracture damage is quite different. The tensile cracks are<10 µm and associated are small debonded regions ranging from 3 to 10 µm in size. Overall the film adhesion to the thermally oxidised titanium is superior to the as-received.

4 CONCLUSIONS

Based on the above experimental results of the GT organically modified coatings on various metallic substrates, conclusions can be summarized as follows:

- The typical inorganic sol-gel coating, TS, displays characteristic transverse cracking of a brittle coating whereas modification by the organic substituent, GTMS, induces a transition in film cracking to a quasi-plastic response and an improvement in the adhesion behavior.
- The fracture and debonding of the GT film is modified by the introduction of thermally grown oxide layers on the metal substrates. For copper and titanium an oxide layer tends to improve the coating adhesion. By contrast the adhesion of GT to the as-received aluminum surface is excellent but degrades markedly when a thick oxide is present. At this point, we can expect that the observed enhancement of the adhesion may come from the new bondings at the sol-gel/metal oxide interface. But also we must consider that, if the roughness of the thermal oxide would increase (with thickness), then it could produce an opposite effect, weakening the interface [15]. Actually this work is in progress: different spectrometry techniques may clarify the last mentioned points, then allow to estabilish well defined correlations.

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