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Mechanical properties and adhesion characteristics of hybrid sol–gel thin films

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Abstract

The hardness and Young's modulus of organic–inorganic hybrid coatings, synthesised using sol–gel technology, deposited on silicon and copper were determined using indentations at low forces with a spherical tipped indenter and found to depend strongly on the size of the organic substituent. The indentation creep response of the coating systems was compared based on fast loading rates and for different times at maximum load. The adhesion characteristics of the coatings on copper were examined to ascertain the influence of the organic substituents on the film cracking behaviour and debond tendencies. For this purpose, coated tensile test specimens were strained uniaxially in a universal testing machine while the surface was examined using an optical microscope. The mechanical response was analysed from the multiple cracking patterns observed and the extent of film delamination from the underlying substrate. The results indicate that the interfacial adhesion and film toughness are dramatically affected by the nature of the organic substituent.

Keywords: Adhesion; Fracture; Sol–gel; Nano-indentation; Elastic properties; Creep

1. Introduction

Thin sol–gel derived silica coatings show considerable potential in modifying the functional behaviour of metal and polymer surfaces. These ceramic coatings provide enhanced protection or passivation of the substrate surface particularly in high abrasion and corrosion environments [1–4] while maintaining the desirable properties of the bulk material. Yet the mechanical integrity and reliability of sol–gel ceramic coatings for many practical applications is largely influenced by the intrinsic properties of the coating and adhesion characteristics with the substrate material, which, in turn, are controlled by the sol–gel processing parameters [5]. Fracture and delamination of the coating from the substrate often leads to catastrophic failure for the component, which can prove to be very disruptive especially in microelectronic devices and protective coatings [6]. Therefore, gaining an understanding of adhesion performance by measuring the interfacial adhesion properties of thin film coatings becomes essential in determining the most effective film/substrate system for a given application.

Recent studies have shown that processing sol–gel hybrid inorganic–organic materials, termed organically modified silanes or ORMOSILS, produce "nano-composite" thin films which possess unique property combinations of the inorganic (hard, brittle) and the organic (soft, flexible) while maintaining optical transparency [7,8]. The main advantage of employing these hybrid coatings is their capacity to adjust their mechanical properties through judicious control of the chemistry and processing variables, including the ratio and nature of the organic and inorganic structural units, solution pH, hydrolysis ratio and drying and

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heating temperatures. Despite recent developments with this promising new class of materials, few studies have been aimed at systematic analysis of coating mechanical properties and adhesion to substrates, especially in terms of the nature and size of the organic group.

The requirement to measure and probe the mechanical properties of thin films can be performed by instrumented submicron indentation tests. Using this technique, the hardness, elastic modulus and creep properties of very thin coatings (thickness <1 μm) can be reliably obtained. This knowledge of the intrinsic film properties is highly valued for both optimising the materials processing and for material selection for specific applications. Further, ascertaining the adhesion of the coating to the substrate material can be determined using simple tensile testing of flat "dog-bone" metal or plastic samples containing the desired coating. The method is simple yet powerful and has direct relevance to film fracture resistance and decohesion, providing significant insights into adhesion behaviour [9–11]. This test has been applied to study the evolution of cracking of brittle films on ductile substrates in situ during straining of the material using optical microscopy and scanning electron microscopy (SEM) [6,7,9,12].

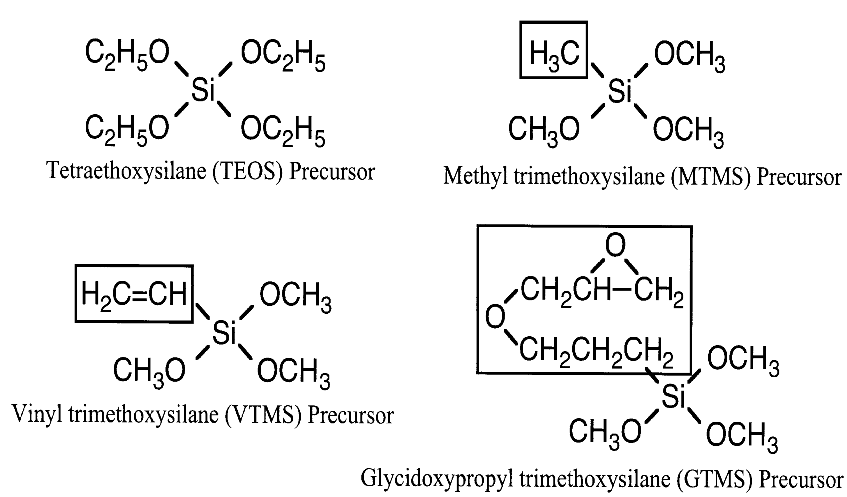
In this work, instrumented nano-indentation and tensile testing were used to probe the mechanical properties (hardness, Young's modulus and creep) and adhesion characteristics, respectively, of a range of thin hybrid sol–gel coatings containing different organic modifiers of varying sizes deposited on silicon and copper substrates. The relationship between the morphology of the coatings and their mechanical properties is studied. Characterisation of the coating fracture and debonding from tensile testing is achieved primarily by in situ examination using optical microscopy, with postmortem SEM of the same coating/substrate specimens providing details of the key differences in coating fracture and damage.

2. Experimental method

2.1. Processing

Sol–gel coating solutions were prepared by adding a 0.01 M solution of nitric acid (HNO_3) to equimolar mixtures of tetraethylorthosilicate (TEOS) and selected alkyltriethoxysilanes in dry ethanol with equivalent SiO_2 concentrations of 5 wt.%, specifically, methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS) and glycidoxypropyltrimethoxysilane (GTMS). A solution of 100% TEOS was also prepared as the control. A water-to-alkoxide ratio (W) of 10 was used in all cases and the solutions were aged at room temperature for 24 h before use. The chemical structures of the organic constituents are given in Fig. 1. The solutions were produced and applied in a class 1000 clean-room to minimise dust contamination, which can act as potential stress–concentration sites for crack nucleation and film delamination. Film deposition onto silicon wafers (25.4 mm diameter; thickness, 0.5 mm; single-sided polished) and polished pure copper coupons (length, 33 mm; width, 3 mm; thickness, 0.45 mm) was carried out by spin coating at 5000 rpm for 2 min. The coated specimens were then allowed to dry for 24 h at 60 °C. The low drying temperature was used to avoid decomposition of the organic species. TG-DTA analysis determined that the decomposition of the organics occurs at less than 350 °C.

The average thickness and refractive index of the films deposited on the silicon wafers was determined using ellipsometry (Rudolph AutoEL, fixed wavelength $\lambda = 632.8$ nm) at five discrete locations on each sample. Thickness measurements of coatings on copper indicated similar values. A scanning probe microscope (D3000, Digital Instruments) operating in tapping atomic force microscopy (AFM) mode was used for ascertaining the surface roughness and morphology of film surfaces. For the measurements, a



(organic modifier group shown in box)

Fig. 1. Chemical structures of the inorganic TEOS precursor and the organic precursors, MTMS, VTMS and GTMS used in the work.