Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 54 (2006) 5469–5475
Acta MATERIALIA
www.actamat-journals.com

Nanoindentation and nanoscratch profiles of hybrid films based on (γ-methacrylpropyl)trimethoxysilane and tetraethoxysilane

Xingwen Zhang [a,b], Lijiang Hu [a,*], Dezhi Sun [b]

[a] Department of Applied Chemistry, Harbin Institute of Technology, Box 713, Harbin 150001, China
[b] Department of Environment Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Received 5 November 2005; received in revised form 25 May 2006; accepted 30 June 2006
Available online 25 September 2006

Abstract

Based on silsesquioxanes (SSO) derived from the hydrolytic condensation of (γ-methacrylpropyl)trimethoxysilane (MPMS) and tetraethoxysilane (TEOS), hybrid films were prepared using the sol–gel process. Nanoindentation and nanoscratch tests were carried out to study the influence of different amounts of TEOS in the hybrid films on testing profiles. The film containing an adequate amount of TEOS (20 wt.%) was found to possess the best elasto-plastic behaviour based on the profiles in the four regions, including the surface, a maximum value, a constant value and a substrate-effect region, as well as the best scratch resistance based on the scratch profiles in the three regions, including the surface, the residual depth and the fluctuation regions. The morphology and the critical load of the film were also provided for evidence.

Keywords: Silsesquioxanes; Sol–gel; Coating; Atomic force microscopy; Nanoindentation

1. Introduction

Performed in the presence of water with an acid or base as a catalyst [1,2], the hydrolytic condensation of trialkoxysilanes, RSi $(OR')_3$, leads to products that are generically called silsesquioxanes (SSO) [3] or polyhedral oligomeric silsesquioxanes (POSS) [4]. These hybrid materials are applied as coatings on substrates in order to enhance abrasion or scratch resistance [5–7], which requires an increase in hardness while maintaining a low brittleness index value (defined as the ratio of hardness to the Young modulus). Hardness can be increased by the addition of colloidal silica or a tetraalkoxysilane to the initial formulation [8,9], resulting in a much more rigid structure which also results in increased brittleness. Therefore, adequate amounts of the modifiers to obtain a hard and tough coating were investigated [10,11].

An interesting type of organically modified silicates (ormosils) is based on the hydrolytic condensation of a tetraethoxysilane (TEOS) with a trialkoxysilane having an organic moiety with a polymerizable group (epoxy, vinyl, etc.) [12,13]. In these kinds of hybrid materials, two different types of networks may be formed: (1) an organic network produced by the crosslinking of the polymerizable groups; and (2) an inorganic network based on Si–O–Si bonds [14]. The fraction of TEOS in the initial formulation determines the prevalent network in the final structure, which in turn determines the resulting mechanical properties (hardness, elastic modulus, scratch resistance) of the hybrid materials.

The continuous stiffness measurement (CSM) technique of nanoindentation testing has been developed over the last decade to determine the mechanical properties of very thin films and coatings [15–19]. This technique allows a continuous measurement of hardness and elastic modulus during loading. A nanoscratch test using a CSM technique [20] and atomic force microscopy (AFM) [21,22] is

* Corresponding author.
E-mail address: hulijiang@vip.sina.com (L. Hu).

1359-6454/$30.00
doi:10.1016/j.actamat.2006.06.057

commonly used to characterize the films and coatings for scratch resistance in preference to other techniques such as a microwedge scratch test (MWST) and scratch tests in macroscopic experiments [23,24]. The CSM scratch test technique can apply a fairly controlled low load to the tip and precise movement of the tip relative to the film. By using a diamond tip to traverse the surface of the films with loads of micronewtons, the contact in the interfaces between the film and particles could be simulated. The scratch depth at a given load or the load at which material fails catastrophically is a measure of scratch resistance. A typical scratch experiment consists of three steps: (1) approaching the surface (pre-scan); (2) translating the sample at ramping loads (scratch scan); and (3) final unloading of the tip (post-scan) [25,26].

In previous work [27], the hardness and elastic modulus of the hybrid films which are based on (γ-methacrylpropyl)-silsesquioxane (MP-SSO) and modified with TEOS as measured by the nanoindentation technique were reported. In this work, the focus was on the effect of the modifier contents on a nanoscratch performance for the MP-SSO films modified with TEOS, and the aim was to determine whether abrasion or scratch resistance could be improved by varying the amount of additional TEOS.

2. Experimental

2.1. Materials

Commercial (γ-methacrylpropyl)trimethoxysilane (MPMS; Dow Corning Z-6030) and tetraethoxysilicate (TEOS; Aldrich) were used in the study of hydrolytic condensation and modification reactions. Formic acid (88 wt.%) was employed as a catalyst. The solvent selected for the final step of the hydrolytic condensation of MPMS and TEOS was ethanol (purity 99.7%). Benzoyl peroxide (BPO; ATOFINA Chemicals 17998-1), an analytical grade reagent, was chosen as a hardener.

2.2. Sol preparation

For the hydrolytic condensation reaction, beakers were prepared containing MPMS and 0, 5, 15, 20, 25 and 30 wt.% TEOS. Ethanol was added to give a 3:1 molar ratio with respect to Si. The polycondensation was carried out in the presence of formic acid, added in a 0.5:1 molar ratio with respect to Si. The corresponding molar ratio of water was 1:1. The beaker was sealed with a plastic film and left for a day at 35 °C. Needle-sized holes were then made in the plastic film and the reaction was continued for another day at the same temperature. Finally, the plastic film was removed and the reaction continued for one more day at 65 °C. The reaction products were homogeneous viscous liquids that could be completely dissolved in different solvents such as tetrahydrofuran, chloroform and ethanol. The TEOS-modified SSO based on MPMS is denoted as MST.

2.3. Coatings on glass substrates

First, the resulting MST was diluted with ethanol (99.7%) in a weight ratio 1:30 and then BPO was added to the solution in a weight ratio 1:100 with respect to the MPMS. Next dip-coating was performed on glass substrates (76.4 mm × 25.2 mm × 1.2 mm) at 270 mm/min. Finally the coated glasses were cured in an oven at 80 °C for 6 h, then at 120 °C for 2 h and finally at 150 °C for a further 2 h. Coatings based on MST are denoted as f-MST, and f-MST with different TEOS contents are denoted as f-MST$_{i\%}$ ($i = 0$, 5, 15, 20, 25 and 30).

The thickness of the f-MST (700 nm) was determined using a Hitachi S-570 scanning electron microscope. The transparency of f-MST in the wavelength range between 190.0 and 3200.0 nm was measured by a Shimadzu UV-3101PC scanning spectrophotometer.

2.4. Nanoindentation and nanoscratch testing

The hardness and elastic modulus of the coating systems were determined using a Nano Indenter XP® (MTS Systems Corporation), incorporating the CSM technique. A triangular pyramid Berkovich indenter was used to fabricate the tip radius. Its indent shape and side view angles were 65.3° and 12.95°, respectively. The Poisson ratio of the hybrid coatings was estimated as $v = 0.225$. Because it enters as $(1 - v^2)$ in the calculation of elastic modulus, an error in the estimation of the Poisson ratio does not produce a significant effect on the resulting value of the elastic modulus [27].

Using the set of experimental curves obtained for every type of coating, average values of hardness and elastic modulus as a function of displacement were generated, together with the corresponding standard deviations.

Both the harmonic frame stiffness and the frame stiffness correction were 0 N/m. Loading was controlled such that the loading rate divided by the load was held constant at 0.05 s^{-1}, and the unloading in stiffness calculation was 50%. Tests were performed in a clean-air environment with a relative humidity of approximately 30%, while the temperature was kept constant at 23 ± 0.5 °C. Equations used to determine hardness and elastic modulus from experimental data are available in the literature [16,20].

Scratch testing was measured using a Nano Indenter XP® system with options for lateral-force measurements. The procedure was similar to that presented in detail elsewhere [28,29]. Before scratching, an initial surface profile of the samples was detected by pre-scanning the surface with the indenter under a low load of 100 μN. Depths of scratches with increasing scratch length were measured in situ by profiling the surface of the film before, during and after the scratch test, resulting in a total length (pre-scan track) of 657 μm for the test while the scratch length (scratch scan) was 563 μm as applied to all f-MST$_{i\%}$. The test was repeated several times for each system. The normal indenter load was linearly ramped from the minimum to