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An energy method to analyze through thickness thin film fracture during indentation

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Abstract

Nanoindentation was utilized to induce fracture of brittle thin oxide films on compliant substrates. The energies were calculated from integrating the resulting load–depth curves from indentation. The total energy applied to the system is a superposition of the energy to deform the substrate and the energy to fracture the film. The applied energy to deform the compliant substrate was separated from the energy applied to the film/substrate system resulting in the energy to fracture the film. The energy for fracture was then converted to a crack extension force and a stress intensity using linear elastic fracture mechanics. The toughness of thermally grown aluminum oxides is between 0.37 and 0.83 MPa $m^{0.5}$, and tends to decrease as film thickness increases over the range of 25 to 63 nm.

Keywords: Thin films; Fracture; Energy

1. Introduction

Hard thin films on soft substrates, such as Al_2O_3 on Al and TiO_2 on Ti, readily form on the surface under ambient conditions. In addition, these films can be grown by anodic methods to produce desirable properties for wear or corrosion resistance. Mechanical breakdown of these films can cause premature failure of the substrate. The most common types of mechanical testing of these films are scratch or peel testing. Recently, nanoindentation has been used to test the mechanical properties of hard thin films such as the elastic modulus and hardness. An appealing use of the nanoindentation method would be to evaluate the fracture toughness or the strain energy for failure in thin film systems by inducing fracture in the film upon loading. A fracture of a film on a substrate may result in a discontinuity in the load–depth curve, and by recording the depth and load at which this discontinuity during the nanoindentation process occurs, it is possible to quantify the fracture process. Thin films have been shown to fracture during indentation processes at critical loads and depths [1]. Previous studies have analyzed these fracture events by calculating an applied radial stress at fracture [2–4], applied stress intensity at fracture [4–7] and the amount of energy required to produce cracks in the film [8–13].

A certain amount of energy is required to fracture a thin film. This energy can be determined by producing a load–depth curve from nanoindentation until fracture occurs. The total energy applied during the indentation can be calculated by simply integration to the fracture depth. The energy used to plastically deform the substrate must be subtracted from the total energy, leaving the amount of energy needed to fracture the thin film.

Malzbender and de With [8] demonstrated that the dissipated energy was related to the fracture toughness of the coating and interface by performing simple integrations of the loading and unloading portions from indentation to determine the amount of energy needed to damage the film. The films that they produced were shown to delaminate and chip along with through thickness fracture in the film. They then calculated the energy needed for delamination and chipping. The crack extension force was then used to calculate the interfacial stress intensity and critical stress intensity for fracture. The plastic deformation in the substrate was not taken into account, leading to an overestimation of the energy release rate.

Other studies have suggested that the fracture energy could be estimated as the energy consumed during the first circumferential crack during the load drop or plateau on the load–

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displacement curve [7,9,11,14]. Three different methods have discussed estimation methods for the fracture energy from the load–depth curves. Li et al. [11] suggested an approach based on the idea that the total energy released during crack initiation is the fracture energy divided by the new surface area. The total energy measured from the load–depth curve was determined by extrapolating the initial loading curve to the depth at which the excursion ended, and the loading curve beyond the excursion back to the depth at which the excursion initiated, and determining the area between these curves over the depth range from the beginning to end of the excursion. Work performed by van der Varst and de With [9] used an internal variable theory to separate the different activities that produce total dissipated energy. The extent of damage at the interface, plastic deformation in the system, damage in the system, and the generation of heat were taken into account. They used such internal variables as crack length, plastic strain, and degree of micro damage to derive a work function that only depended on the initial and final states to determine the energy. The surface roughness was found to increase the scatter in the data. However, the data was seen to follow a master curve. The indentation in the sample produced circumferential cracking outside the contact area of the tip. The work from the ring cracking was calculated by multiplying the load at the discontinuity by the discontinuity length and dividing by the surface area of the crack. This does not take into account the effects from the substrate and the energy calculated is an overall dissipated energy from the system, not just the film. The third energy method suggested by Abdul-Baqi and Van der Giessen [10] was to multiply one half of the cracking depth by the load jump.

Numerical simulations performed by Abdul-Baqi and Van der Giessen [10] demonstrated that the energy determination by Li et al. [11] underestimated the overall energy for small fracture energies and small film thicknesses, where the methods by Abdul-Baqi et al. and van der Varst et al. were reasonable estimations. However, the second and third methods overestimate the overall energy for large fracture energies and large film thicknesses. The problem with these methods is that the loading is assumed to be linear with depth. However, the indentation follows elastic–plastic contact theories where the load and depth have a power law relationship [15,16]. Also, substrate effects were not taken into account for any of the above methods to determine the energy to initiate a crack.

The current study will outline a method to separate the energy dissipated from fracture of the film and the energy dissipated to plastically deform the substrate. Being able to separate these energies from the total energy applied by the nanoindenter allows a determination of the energy release rate for film fracture and for calculating the critical stress intensity factor under plane strain.

2. Experimental procedure

Grade II polycrystalline titanium with a primarily α HCP grain structure was ground to 600 grit and then mechanically polished using 0.05 μm colloidal silica. A thin oxide was then anodically grown using an EG and G 173 and 175 potentiostat and controller. The film was grown in a 0.1 M H_2SO_4 solution. The final potential was reached using step polarization. The potential was increased by 1 V every few minutes (once the current density stabilized at each potential) until a maximum of 9.4 V was reached. The potential was measured against an Ag/AgCl reference electrode, and a graphite counter electrode was used to accommodate current flow. The sample was then held at the maximum potential for 5 min. The titanium oxide thickness was determined using X-ray photoelectron spectroscopy (XPS) depth profiling with a sputter rate calibrated against known thicknesses of SiO_2 on Si [2]. The thickness of the oxide was measured by determining the depth at which the oxygen is 50% of its maximum concentration. The film thickness was found to be approximately 250 nm.

Two different aluminum substrates were also tested in this study. The samples were made from a commercially available ingot of 1100 series aluminum and a 99.99% pure Al ingot. The substrates were encapsulated in an evacuated quartz tube, back filled with argon gas and annealed at 500 °C for 24 h.

After annealing, the aluminum samples were polished. One set of samples from the 1100 series and 99.99% pure aluminum were mechanically polished by grinding the samples to 1200 grit and then polishing to 0.05 μm with colloidal silica. Another set of samples from the 1100 series was electropolished in an electrolyte of 25% nitric acid and 75% methanol at −20 °C using a bias of 10 V. After polishing, different film thicknesses were obtained by thermally growing oxides at 500 °C for 1, 2, and 3 h and air quenching at room temperature. The oxide growth was shown by Aylmore et al. to follow a linear law with time between 500 and 550 °C [17]. Using the linear law, the theoretical film thickness should be 35 nm, 50 and 65 nm for 1, 2, and 3 h growth time at 500 °C, respectively. The oxide thickness as measured using a Gaertner spectral ellipsometer, and were determined to be 25, 54, and 63 nm for 1, 2, and 3 h growth times, respectively. The oxide thickness was not influenced by the underlying substrate in these materials. Gulbransen and Wysong studied the growth of aluminum oxide on aluminum over a temperature range of 400 to 500 °C for 30 min, and found the oxide layer to be amorphous [18,19]. The anodic aluminum films were grown on the 1100 aluminum alloy in a 15 wt.% sulphuric acid electrolyte using a 12 V potential and a current density of approximately 150 A/m^2 for approximately 5 min. The anodized aluminum samples were mechanically polished and cleaned in a caustic NaOH solution prior to film growth.

Nanoindentation was carried out using a Hysitron Triboscope coupled with a Park Autoprobe scanning probe microscope. The indentations were made with a cube corner diamond indenter (90° included angle) with an effective tip radius of 570 nm. The tip radius was calculated by performing a series of elastic loading curves in tungsten, and then calculating a tip radius using curves using the Hertzian elastic loading profile [15]. While this tip radius is significantly blunter than most cube corner tips in the as purchased condition (many of which are nominally 50 nm) we have found that significant tip blunting occurs over a period of several years, particularly when carbide forming materials such as W and Fe are regularly