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Improved adhesion of Au thin films to SiO_x/Si substrates by dendrimer mediation

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Abstract

Quantitative evidence of significantly improved interfacial adhesion between Au films and SiO_x/Si substrates induced by an organic dendrimer monolayer was presented. For dendrimer-mediated Au films, nanoscratch tests revealed a critical load that was two times higher than that for films without dendrimer mediation. Atomic force microscopy (AFM) examination of nanoindents revealed much constrained lateral flow of metals in the dendrimer-mediated Au films during nanoindentation, indicating enhanced adhesion due to the presence of the dendrimer layer.

Keywords: Adhesion; Dendrimer; Au film; Nanoscratch

1. Introduction

Poor adhesion between gold films and oxides is well known [1,2]. Although Au adhesion to oxides can be improved by introducing metallic interlayers, such as tantalum or chromium [1], this method suffers from some undesirable effects, in particular alloying and interdiffusion. Recently, Baker et al. [3] showed that interfacial adhesion between Au films and glass or Si substrates could be improved by substituting a thin organic layer, such as amine-terminated polyamidoamine (PAMAM) dendrimer for the metallic underlayer [3]. Results from peel tests revealed qualitatively improved adhesion by the PAMAM dendrimer, with the most marked effect exhibited by the Generation 8 (G8) dendrimer [3]. Introduction of the G8 dendrimer also influenced the nanoindentation response of Au films. Street et al. [4] found that dendrimer-mediated Au films on silicon wafers covered by native oxides (hereafter indicated as SiO_x/Si) were more resistant to indentation penetration than dendrimer-free films. However, detailed attempts to quantify the adhesion improvement via dendrimer-mediation and related deformation characteristics are still lacking.

This paper reports our recent investigations of dendrimer-mediated adhesion of Au films to SiO_x/Si substrates. Experimental results obtained from nanoscratch tests, scanning electronic microscopy (SEM), nanoindentation, and atomic force microscopy (AFM) are presented.

2. Experimental details

Two inch (50.4 mm), (100)-oriented silicon wafers, Si(100), with a layer of native oxides (SiO_x) were used in this study. The thickness of the SiO_x layer was ~2 nm, as previously determined by X-ray reflectivity (XRR [4]). To investigate dendrimer-mediated adhesion, some of the SiO_x/Si wafers were covered by a self-assembled monolayer (SAM) of G8 amine-terminated PAMAM dendrimer prior to

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Au film deposition. To form the G8 SAM, wafers were first cleaned by placing them in a freshly prepared piranha solution (3:1 H_2SO_4/30% H_2O_2) for 1 h to remove organic impurities. The clean wafers were then placed in a ground-glass-sealed weigh bottle along with a 1 μM ethanolic solution of the PAMAM dendrimer. The substrates were allowed to remain in the solution for 12 h, where a self-assembled monolayer of dendrimer molecules was absorbed stably onto the surface. The substrates were then removed and rinsed in pure ethanol followed by drying in a stream of dry N_2.

Au films were deposited by thermal evaporation using one of two deposition systems, both of which utilize resistive heating of W boats to achieve metal evaporation. The first system, which can hold up to six wafers, is cryopumped with a base pressure of 1×10^{-8} Torr. The second system, which can accommodate one whole wafer, has a base pressure of ~5×10^{-8} Torr. The film thickness 12.5 monitored in situ using a quartz crystal microbalance and confirmed ex situ by XRR analysis [4]. Matched pairs of Au on dendrimer-mediated and dendrimer-free substrates were obtained from the same deposition system. The film/substrate systems will be designated as Au/D/SiO_x/Si and Au/SiO_x/Si, respectively.

Ramped load scratch tests were performed using a Nano Indenter® II instrument equipped with a nanoscratch attachment (MTS Systems, Oak Ridge, TN). A Berkovich diamond tip oriented in the face-forward mode was applied at the rate of 1 μm/s [5–7]. Each scratch test, 100 μm in length, was performed by linearly increasing the normal load from 0.02 mN to the desired level. Both the surface profile and the friction coefficient were recorded in situ. Surface profiles of the scratch before and after testing were also obtained by scanning the tip at an extremely low load (0.02 mN). The morphology of scratch tracks was also examined ex situ by SEM.

Nanoindentation tests were performed on a Hysitron TriboIndenter® system (Minneapolis, MN) using a Berkovich diamond tip. In addition to depth-sensing capability, the TriboIndenter® system is also equipped with an AFM attachment, which allows for in situ imaging of the indentation area, using the same tip as a surface probe. Generally, the AFM imaging is finished within 5 min after the unloading.

3. Results and discussion

Fig. 1 shows two selected surface profiles collected before, during, and after scratching Au/D/SiO_x/Si (Fig. 1(a)) and Au/SiO_x/Si films (Fig. 1(b)), respectively. The surface displacement and the coefficient of friction μ are plotted as a function of scratch travel distance (and the applied normal load). The displacements corresponding to the "during-scratch" profiles are greater than those corresponding to the "after-scratch" profiles in that the former includes all elastic/

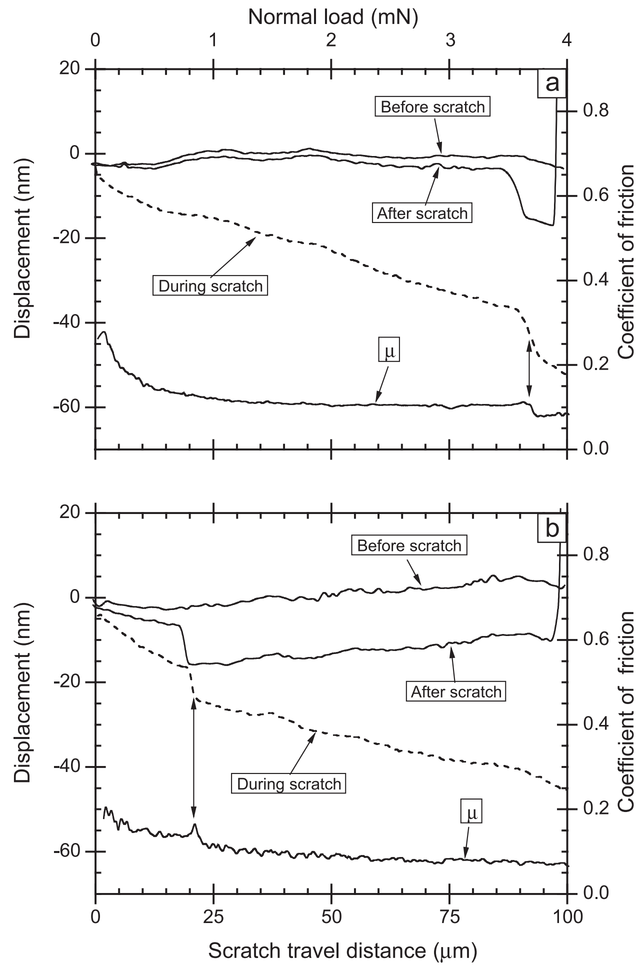

Fig. 1. Ramped load (4 mN) nanoscratch surface displacement and friction coefficient profiles for Au/D/SiO_x/Si (a) and Au/SiO_x/Si (b).

plastic contributions from the entire film/substrate system [5], while the latter mainly reflects the plastic deformation of the film. With an increase of the applied normal load, the Berkovich tip gradually scratched through the sample. In both cases, the profile drops suddenly at a well-defined critical position/load, which suggests film failure [6]. These critical loads (L_c) are marked by the vertical arrows in Figs. 1(a) and (b). The sudden drops at these critical points were also reflected in the μ profiles. The corresponding wear tracks of the two scratches were further examined ex situ by SEM, as shown in Fig. 2. Each track shows a clear critical point, beyond which the track quickly expanded. These critical points indicate the onset of film failure and match well with those shown in the corresponding surface profiles (Figs. 1(a) and (b)). With dendrimer mediation, film failure was delayed (Fig. 2(a)). Accordingly, for the same scratch, both the surface profiles (Fig. 1) and microscopic observations (Fig. 2) lead to comparable critical loads, which are ~3.5 and <1 mN in the systems with and without dendrimer mediation, respectively.

Clearly, dendrimer mediation of the substrate has resulted in a significant improvement in Au film adhesion (i.e., a