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Role of oxide seed layer in plastic response of epitaxially grown textured metal films

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ABSTRACT

The elastic/plastic mechanical behavior of freestanding polycrystalline {111}-textured Pt films with thicknesses 50–1000 nm and different combinations of grain size and film thickness, grown epitaxially on a 35–50 nm thick polycrystalline (100)-TiO_2 (rutile) seed layer, was studied at uniaxial tension strain rates 10^{-6} - 10 s^{-1}. The mismatch strain between the {111}-Pt films and the underlying (100)-TiO_2 seed layer gives rise to an interfacial dislocation network, which, in turn, determines the initiation of plastic deformation in Pt. Experiments showed that the flow stress increases, while the plastic strain accumulation at failure decreases with decreasing Pt film thickness. A modified Thompson model that accounted for the combined effect of film thickness and grain size provided good predictions for the elastic limit of Pt films. However, the yield stress was underestimated by the same model; a Taylor strain hardening model was superimposed to the modified Thompson model to account for additional hardening as a result of dislocation interactions during plastic deformation, which provided good predictions for the evolution of flow stress with plastic strain.

1. Introduction

Metallic thin films in freestanding form or deposited on substrates have been shown to exceed the flow stress of their bulk counterparts: Experiments with face-centered cubic (FCC) Ag, Al, Au, Cu, Ni, Pb films with thicknesses of 50–2000 μm have shown that the flow stress increases with decreasing film thickness [1–9]. In the case of metal films deposited on substrates, mechanistic models have been developed to explain this inverse film thickness dependence of flow stress. Based on the threading dislocation concept by Freund for a film bonded to a substrate with some mismatch strain [10], Nix [11] developed a quantitative model considering the film/oxide and film/substrate interfaces acting as impenetrable obstacles to dislocation motion, thus necessitating the deposition of misfit dislocations at interfaces. Later, Thompson [12] extended the Nix-Freund model to polycrystalline films with grain diameters that are at least twice as large as the film thickness by including grain boundaries (GBs) as additional obstacles to dislocation motion. The two models combined could qualitatively explain the inverse film thickness and grain size dependence of flow stress that was experimentally observed for Al films deposited on Si substrates with an anodic oxide layer at the top surface [2]. Both the Nix-Freund and the Thompson models showed that the film texture influenced the yield stress.

In-situ TEM studies of thermally strained, epitaxially grown, single crystal Al [13] and Cu films [7] on (0001) α-Al_2O_3 substrates revealed the motion of threading dislocations on inclined {111} planes with the eventual deposition of dislocation segments at Al/α-Al_2O_3 and Cu/α-Al_2O_3 interfaces. As a result, the Nix-Freund model could quantitatively capture the flow stress of such epitaxial metal films. It was further observed that epitaxial film-substrate interfaces acted as dislocation sources, and dislocation half-loops were emitted from the interfacial dislocation network. In contrast, no such phenomena were observed in polycrystalline Al and Cu films deposited on amorphous oxide or nitride layers on Si substrates. The amorphous underlayers did not promote the formation of stable interfacial dislocation networks because they

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permitted atomic rearrangements at the interface, thus allowing for dislocation segments arriving at the interface to escape [14]. Consequently, in the absence of interfacial dislocations, the Nix-Freund or the Thompson model underestimated the flow stress in polycrystalline films deposited on amorphous layers [4,5] where the initiation of plastic deformation is delayed due to the scarcity of dislocation sources.

Von Blanckenhagen et al. [15] used the aforementioned idea to model the deformation response of polycrystalline metal films. They considered dislocation sources in polycrystalline metal films to be rare and, therefore, each Frank-Read source inside a grain had to operate several times to generate more dislocations and achieve the resulting plastic deformation. Their approach using discrete dislocation dynamics reproduced the experimentally measured flow stresses in polycrystalline Cu films deposited on amorphous and deformable polyimide layers. Thus, the underlying layer plays a major role in determining the plastic deformation of metal films: source controlled deformation models work well for polycrystalline films in the absence of interfacial dislocation networks, whereas epitaxially grown single crystal metal films are well described by the Nix-Freund model. However, there are hardly any studies on the deformation behavior of polycrystalline metal films grown epitaxially on polycrystalline layers. Although many metal films are deposited on amorphous diffusion barrier layers that are on top of single crystal silicon to prevent formation of metal silicides [16,17], there are cases when polycrystalline metal films are grown epitaxially on polycrystalline layers in order to achieve specific textures [18]. The deformation behavior of such films is expected to be significantly different from that of films deposited on amorphous layers. Furthermore, the Nix-Freund or the Thompson models which should be applicable to epitaxially grown metal films do not model the evolution of flow stress with plastic strain.

This work reports on the plastic response of highly {111}-textured epitaxial polycrystalline Pt films grown on 35–50 nm thick (100)-textured polycrystalline rutile TiO_2 underlayers. It focusses on relationships between the film thickness, grain size, and strain rate vs. the plastic mechanical response of textured Pt films with thicknesses ranging between 50 and 1000 nm in the form of bilayers with an underlying TiO_2 seeding layer. It also aims at addressing the effect of high aspect ratio columnar grain structure, which is not captured by previous models. To this goal, existing dislocation based mechanistic models, modified to account for strain hardening, are applied to predict the evolution of flow stress with plastic strain and are compared with experimental measurements.

2. Experimental methods

Micro and nanometer thick Pt film specimens were fabricated at the US Army Research Laboratory (ARL) in Adelphi, MD using a combination of DC magnetron sputtering and etching on Si (100) substrate. Such Pt films are employed as contact electrodes in lead zirconate titanate (PZT) based Microelectromechanical Systems (MEMS) because they provide a sharp interface that suppresses interdiffusion of Pb and provide an excellent growth template for PZT thin films [19–21].

The fabrication process, described in detail in Ref. [19], began with the deposition of a base layer of Ti on a 500 ± 25 nm thermally grown SiO_2 layer on a silicon wafer to serve as an adhesion layer using DC magnetron sputtering with a 99.99% pure Ti target at 40 °C. The Ti films had strong {0001} texture with a basal plane of hexagonal close packed (HCP) structure lying in the plane of the substrate. The Ti films were then converted into rutile through oxygen annealing for 30 min inside a tube furnace at 750 °C. The TiO_2 films had measured thicknesses of 35 nm and 50 nm and X-Ray diffraction studies showed (100) texture. Next, sputter deposition of Pt was carried out for thicknesses of 1000, 500, 200, 100 and 50 nm onto the TiO_2 with a 99.99% pure Pt target at substrate temperature of 500 °C, as shown in step (A) in Fig. 1(a). The resulting {111}Pt||(100)TiO_2 grain-to-grain heteroepitaxy has been established before for 100 nm thick Pt films [18,19] with the underlying (100)-textured TiO_2 acting as the seed layer for the growth of {111}-textured Pt.

Patterning of the Pt films to specimen geometries and dimensions was done using Ar ion milling, as shown in steps (B) and (C). Prior to isotropic etching of the Si substrate to release the test structures, the wafer was exposed to a 20 s reactive ion etching with CHF_3 and O_2 to remove the surface oxide developed on the exposed silicon surfaces. Next, the film was subjected to xenon difloride (XeF_2) isotropic etching to remove the Si underneath as shown in step (D). Finally, freestanding Pt/TiO_2 bilayers were prepared by treatment with a solution of buffered hydrofluoric acid (HF) which removed the SiO_2 layer, step (E). After release, the wafer was diced using Mahoh dicing from Accretech America to prepare individual dies containing dog-bone bilayer specimens with 1035 nm and 535 nm thicknesses, Fig. 1(b), and micro-tensile specimens of 250 nm, 150 nm and 100 nm thickness, Fig. 1(c). The dog-bone specimens had gauge width and length of 100 and 1000 μm, respectively, whereas the tested micro-tensile specimens had three different gauge widths of 13, 19 and 30 μm, and lengths varying in the range of 150–350 μm.

A custom-built microscale tension apparatus for freestanding thin films, described in detail in Ref. [22], was employed to apply strain rates in the range of 10^{-6} to 10^{1} s^{-1}. Full-field strains were derived by application of digital image correlation (DIC) to images of the specimen surface recorded with an optical microscope at frame rates as high as 30,000 fps. In order to compute strains, a random speckle pattern was deposited on the films by dispersing 1-μm Si particles [22].

3. Results and discussion

3.1. Microstructure, surface morphology and texture characterization

Focused ion beam (FIB), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) studies were conducted to determine the thickness, average in-plane grain size as measured at the film's top surface, surface morphology and texture of the Pt films, respectively. The mean grain size and standard deviation were measured from SEM micrographs, such as those shown in Fig. 2(a-e), by using the intercept method and taking into account ~2000 columnar grains in each film. The unimodal in-plane grain size distribution curves in Fig. 2(f) fit log-normal distribution functions well and and demonstrated broadening with increasing film thickness. As shown in Table 1, the average in-plane grain size scaled with Pt film thickness, which may be due to a specimen thickness effect [23] occurring as a result of pinning of GBs by surface grooves when the mean size of columnar grains approaches the film thickness [24]. Studies have also revealed that GB grooving affects the grain size distribution of stagnant grain structures in thin films, as for example in the case of pinned GBs, and these distributions are well described by log-normal probability distributions [25,26]. It may be noted that previous studies on Pt films reported in-plane grain sizes of 20–50 nm [27], 25 ± 3 nm [22], and 25 ± 10 nm [28] for 450 nm, 400 nm and 450 nm thick films, respectively. These small grain sizes reported previously were due to film deposition at substrate temperature of 50 °C (~0.15 $T_{m,Pt}$); it has been suggested that at these low homologous temperatures, continued "renucleation" of