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Epitaxial growth of Cu(100) and Pt(100) thin films on perovskite substrates

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Abstract

Pulsed laser deposition has been used to grow epitaxially oriented thin films of Cu and Pt on (100)-oriented $SrTiO_3$ and $LaAlO_3$ substrates. X-ray diffraction results illustrated that purely epitaxial Cu(100) films could be obtained at temperatures as low as 100 °C on $SrTiO_3$ and 300 °C on $LaAlO_3$. In contrast, epitaxial (100)-oriented Pt films were attained on $LaAlO_3$(100) only when deposited at 600 °C. Atomic force microscopy images showed that films deposited at higher temperatures consisted of 3D islands and that flat, layered films were obtained at the lowest deposition temperatures. Importantly, Cu films deposited at 100 °C on $SrTiO_3$(100) were both purely (100)-oriented and morphologically flat. Pt and Cu films displaying both epitaxial growth and smooth surfaces could be obtained on $LaAlO_3$(100) only by using a three-step deposition process. High-resolution transmission electron microscopy demonstrated an atomically sharp Cu/$SrTiO_3$ interface. The crystalline and morphological features of Cu and Pt films are interpreted in terms of the thermodynamic and kinetic properties of these metals.

Keywords: Copper(80); Platinum(375); Physical vapor deposition(370); Epitaxy(124)

1. Introduction

The growth of thin metal films is of considerable scientific and technological interest, since supported metals are currently in wide use as electrodes, interconnects, magnetic layers, and catalysts [1–6]. For metal films to be of practical use, it is very important to have control over their crystalline properties (orientation, grain size) as well as morphological features (3D particles or flat layers). In many instances, these metal films must be integrated with ceramic or semiconducting substrate layers, but the general characteristics of metal/ceramic interfaces are unfortunately still not well understood [1]. Epitaxial growth of metal thin films on ceramic substrates can provide insight into interfacial bonding, surface quality, strain, and other factors that can affect the properties of metal thin films in multilayer structures.

The chemical inertness of Pt, particularly its stability against oxide formation, has made it a popular choice for studying metal films grown on ceramic substrates. Pt thin films have been deposited epitaxially on a number of single crystal ceramic substrates with low-index orientations, including $SrTiO_3$(100) [7–9], (110) [10], and (111) [11], and MgO(100) [12–19], using a variety of deposition techniques. Cu is another attractive choice as a thin metal film because it is used in thin film form as electrical interlayers [2,3] and supported catalysts [20,21], and is quite inexpensive compared to Pt. A number of studies exist describing the epitaxial growth and interface structure of Cu on single crystal sapphire(0001) [22–25], Si(100) [26–32], and Si(111) [29–33] substrates, as well as textured growth on glass substrates [32–35]. However, very few detailed studies exist describing Cu heteroepitaxy on commonly used cubic ceramic substrates like MgO [36] or $SrTiO_3$ [37,38].

In the present work, single-crystal, (100)-oriented cubic $SrTiO_3$ and $LaAlO_3$ were chosen as substrates to take advantage of their close structural matches with Cu and Pt and promote heteroepitaxial growth. The metals are both face-centered cubic (fcc) and the oxides each adopt the perovskite structure, which can be considered to be an fcc derivative. Furthermore, the lattice parameters of the materials are quite similar: Cu (a = 0.3615 nm) has a lattice mismatch of 8.0% with $SrTiO_3$ (a = 0.3905 nm) and just 4.8% with $LaAlO_3$ (a = 0.379 nm) (see Ref. [39]). Likewise, Pt (a = 0.3924 nm) has a lattice mismatch of just −0.5% with $SrTiO_3$ and −3.4% with $LaAlO_3$. These structural similarities between the metals and

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the (100)-oriented oxide substrates should promote the epitaxial growth of (100)-oriented films.

Both the crystalline and morphological characteristics of epitaxial thin metal films grown on ceramic substrates exhibit a clear temperature dependence; higher temperatures promote crystalline epitaxy and 3D island growth, while lower temperatures lead to randomly oriented (or (111)-textured), flat films. This work will demonstrate that (100)-oriented Cu films having flat surface morphologies can be obtained at a single deposition temperature, and that multi-step processing methods allow for such growth in other metal/perovskite systems. We discuss the roles of the intrinsic properties of Pt and Cu (surface diffusion rate and surface energy anisotropy) and processing characteristics (deposition temperature and rate) in determining film microstructure and surface morphology. These factors can offer insight into the kinetic and thermodynamic processes taking place during metal deposition. An improved understanding of the relevant factors in metal/ceramic heteroepitaxy will allow for the prediction of growth characteristics and the selection of appropriate metal and ceramic materials for use in thin film structures.

2. Experimental details

Polished single crystal substrates of $SrTiO_3$(100) and $LaAlO_3$(100) (miscut angle $<0.5°$) were obtained from Crystal GmbH. Prior to film growth, all substrates were ultrasonically cleaned in acetone, followed by ethanol, for 5 min each. Samples were then etched 4 min in a 3 : 1 HCl : HNO_3 solution, rinsed with distilled water, dried with a heat gun, and annealed 1 h at 800 °C in 13 Pa flowing O_2. This treatment procedure has previously been shown to be effective for producing high-quality low-index $SrTiO_3$ surfaces [9,11,40–43].

Once prepared, substrates were attached to the heating surface with conductive silver paint and placed into the deposition chamber. Samples were heated to the desired deposition temperature in vacuum (<0.1 Pa), maintained by a turbomolecular pump. The deposition atmosphere was established by lowering the turbopump speed and introducing flowing Ar (for Cu) or O_2 (for Pt) gas into the chamber to attain a dynamic pressure of 1.3 Pa. Deposited metal films were cooled in a dynamic vacuum (<0.1 Pa) to prevent post-oxidation. Ar gas was selected for Cu growth to avoid oxidation during growth. Pt is non-reactive, and thus O_2 was selected for its possible surfactant effects [44,45].

Pulsed laser deposition (PLD) was performed using a Compex 201 laser (Lambda Physik). The metal targets were 0.25 mm thick Cu and Pt foils, 99.99% purity from Alfa Aesar. The KrF laser ($\lambda = 248$ nm, pulse duration = 20 ns) was operated at a rate of 3 Hz, with a laser energy density at the target of ≈ 8.0 J/cm^2. The target-to-substrate distance was maintained at ≈ 60 mm in all experiments, and targets were rotated around their centers during the deposition to keep their surfaces fresh. Following a short 5 min ablation (with the substrate shielded), to clean the target surface, Cu or Pt metal was deposited for 60 min. Reflectometry scans [46] indicated that the Cu films were grown at a rate of $4.0 \pm 0.3 \times 10^{-3}$ nm/pulse, consistent with transmission electron microscopy (TEM) measurements. This rate is considerably slower than that previously observed in our system for Pt ($\approx 18 \times 10^{-3}$ nm/pulse) [47].

The crystal structures of the resultant films were characterized by X-ray diffraction (XRD). Conventional 2θ-θ scans were carried out to determine the crystalline orientation normal to the surface. Cu and Pt films that were confirmed to be (100)-oriented were further examined using a 3-circle diffractometer, which recorded 2θ-θ, ϕ, and ω scans to determine crystalline quality, lattice parameters, and orientation; in-plane epitaxy; and mosaic spread, respectively. Cross-sectional TEM specimens were prepared using standard techniques: grinding of glued sandwich slices, followed by dimple grinding and Ar^+ ion-beam milling. The primary energy of the Ar^+ ions was 3.5 keV with a beam current of ≈ 15 µA. Conventional TEM was carried out using a JEM-2000EX (JEOL) microscope, operated at an accelerating voltage of 200 kV. High-resolution imaging and analysis were performed using a FEI Tecnai F20 (field emission gun) operating at 200 kV and equipped with a Gatan Imaging Filter. Film surface morphologies were analyzed with atomic force microscopy (AFM) using an AutoProbe CP atomic force microscope (Park Scientific Instruments), fitted with a 5 µm scan head for optimal lateral resolution, and operated in contact mode.

3. Results

3.1. Epitaxy of metal thin films

Cu films were deposited on $SrTiO_3$(100) and $LaAlO_3$(100) substrates at temperatures ranging from room temperature (RT) to 600 °C, with the goal of depositing purely (100)-oriented Cu films having flat surface morphologies. The thicknesses of all films were evaluated using X-ray reflectometry, and were found to be in the range of 40–46 nm. XRD results for Cu films deposited on $SrTiO_3$(100) substrates are presented in Fig. 1.

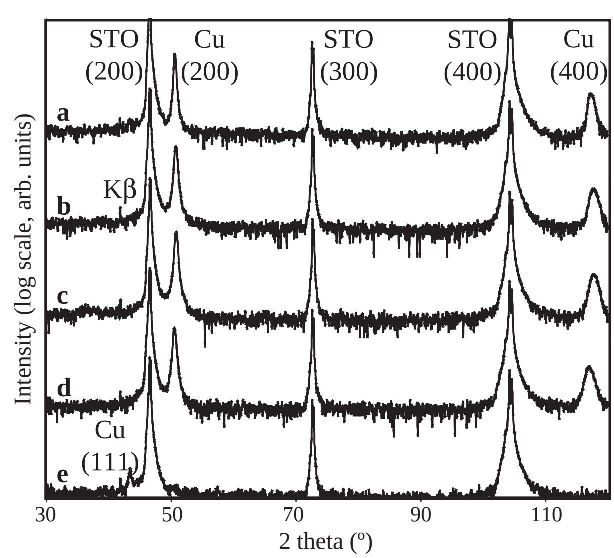

Fig. 1. Normal 2θ-θ XRD patterns for Cu films grown on $SrTiO_3$(100) substrates at (a) 600 °C, (b) 500 °C, (c) 300 °C, (d) 100 °C, and (e) RT.