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Abstract.

The nucleation and coalescence of silver islands on coated glass was investigated by in-situ measurements of the sheet resistance. Sub-monolayer amounts of transition metals (Nb, Ti, Ni, Cr, Zr, Ta, and Mo) were deposited prior to the deposition of silver. It was found that some, but not all, of the transition metals lead to coalescence of silver at nominally thinner films with smoother topology. The smoothing effect of the transition metal at sub-monolayer thickness can be explained by a thermodynamic model of surface energies.

Nucleation and growth are of great importance to numerous deposition processes and practical applications such as silver-based low emissivity coatings. For high transmission in the visible and high reflection in the infrared, it is desirable to utilize very thin silver films of low sheet resistance¹. Very small thickness and low sheet resistance are clearly conflicting requirements demanding careful optimization of the growth process. Sheet resistance is determined by scattering of conduction electrons at defects, grain boundaries, and surfaces. Therefore it is desirable to produce ultrathin films with large aligned grains and very smooth surfaces. However, metal films tend to grow on oxides in Volmer-Weber (island) mode². To improve wetting and promote growth with preferential orientation it is common to coat glass with other transparent materials like TiO₂ or even better with ZnO³. In application with tempered or bent glass, a “sacrificial” interlayer of a few nanometer thickness is used to protect silver from oxidation. The sacrificial material is oxidized in the process and becomes part of the transparent multilayer.⁴ Using much thinner “sacrificial” films, we will demonstrate that the sacrificial material acts as seeds of nucleation for silver which under certain coverage and material conditions can lead to earlier coalescence with greatly reduced surface roughness.

Two deposition methods were used: (i) filtered cathodic arc deposition, and (ii) magnetron sputtering. The setup for filtered cathodic arcs was described in earlier work on coalescence of silver islands⁵ where no sacrificial material was used. In essence, each miniature arc source had a cathode rod of 6.25 mm diameter; the cathode is the feedstock for the metal plasma⁶. The sources (one for Ag, the other for the transition metal)

operated in repetitively pulsed mode with arc pulses of 1.2 kA amplitude, 600 μ s duration, and a repetition rate of 1.6 p.p.s. Each source had a 90° filter to remove unwanted metal debris (“macroparticles”) from the plasma⁷. The chamber was cryogenically pumped to a base pressure of about 10^{-4} Pa; no process gas was needed or used

For the sputtering, 3” magnetrons were used. Silver was sputter in DC mode, whereas the TiO₂ or ZnO:4at% underlayer on glass, if used, were sputtered in reactive mode using an AE Pinnacle Plus at 100 kHz with 1 μ s reverse time. The deposition rates were calibrated ex-situ by measuring step heights of relatively thick films (~100 nm) using a Dektak profilometer. The nominal thickness of ultrathin films was determined by counting arc pulses for the filtered arc process and by timing for the sputtering process after having determined that rates and thicknesses are indeed reproducible. For example, the deposition rate for the filtered arc process of silver was determined to be 0.023 nm/pulse, corresponding to about 1/10 of a monolayer per pulse, while the instantaneous rate was 37 nm/s. For the sputtering process, a low power of only 50 W was selected leading to a deposition rate of 0.75 nm/s. Low power gave us better control of timing the process and the final nominal thickness. It should be stressed that the reported film thicknesses are nominal (they can be sub-monolayer or consist of islands).

The substrates were uncoated standard microscope glass slides or slides pre-coated with reactively sputtered TiO₂ or ZnO:4at%Al. The samples were cleaned with ethanol and deionized water, and dry-blown with nitrogen prior to being mounted on a water-cooled substrate holder. For both pre-coatings and silver coatings, the substrate

temperature was generally near room temperature although the surface was subject to some heating by the deposition process.

The films were evaluated by in-situ sheet resistance measurements and atomic force microscopy (AFM, Nanoscope IIIa). As in our earlier paper⁵, the samples were prepared for in-situ sheet resistance measurements by masked deposition of two silver contact pads such that a square area of 2.5 cm x 2.5 cm was formed between them. Therefore, the measurement of resistance between the pads directly indicated sheet resistance. When the nominal thickness of the growing film between the contact pads exceeded a certain thickness, e.g. 8 nm, a sharp drop of sheet resistance by several orders of magnitude can be observed, indicating the coalescence of islands (Fig. 1). The resistance was measured by either a Keithley 177 or by FLUKE 189 precision multimeter. Possible effects of the measuring current on the result were excluded by repeating the measurements with the instrument disconnected during the deposition process.

The original thrust of the experiments aimed to investigate niobium as a sacrificial material. An initially surprising result was found when using unusually thin films. Nominally 0.1 nm thick Nb film had a much greater modifying effect than a nominally 0.2 nm thick film (Fig. 1). Repetition of the experiment confirmed this observation.

AFM measurements revealed that nominal 0.1 nm of Nb led to much smoother, fine-grained silver films than 0.2 nm of Nb (Fig. 2). The RMS roughness was about the same for the samples without and with 0.2 nm Nb (2.9-3.2 nm), and much reduced for the 0.1 nm Nb samples (only 0.8 nm).

The experiments were continued focusing on the industrially more relevant sputtering method. When using very small amounts of niobium, nominal 0.1 and 0.2 nm, coalescence of silver occurred earlier as compared to deposition without this material, however, 1 nm of Nb had the opposite effect. We found again the same effect when switching to Ti as the seeding layer material (Fig. 3).

Further experiments with Ni, Cr, Zr, Ta, and Mo showed that the effect on coalescence was not always the same, not even qualitatively. For some materials, such as Cr, coalescence of silver islands was delayed, i.e. occurred at greater nominal silver thickness, even when very small amounts of the seed material were used.

To understand why small amounts of transition metals affect the growth of silver in a very different fashion, depending on surface coverage and kind of material, one should consider the thermodynamic driving forces that determine two or three dimensional growth. Minimization of Gibbs free energy in a thin film system requires considering the metal-oxide interfacial free energy and the metal surface free energy. The growth mode under thermodynamic equilibrium conditions is determined by

$$\Delta\gamma = \gamma_{metal} + \gamma_{metal-substrate} - \gamma_{substrate} \quad (1)$$

where γ_{metal} , $\gamma_{metal-substrate}$, and $\gamma_{substrate}$ are the free energies of metal surfaces, metal-oxide substrate interfaces, and the oxide substrate surfaces, respectively. If $\Delta\gamma > 0$, 3D island growth occurs; otherwise, 2D layer growth is thermodynamically preferred (Bauer's criterion).

Studying $TiO_2(110)$ -metal systems, Hu and coworkers⁸ have shown that the issue of island versus layer growth modes can be classified via the relation of the heat of formation of metal oxides and the heat of sublimation of metals, i.e. parameters

representing the strength of metal-oxide interfacial interactions and the strength of metal/metal lateral interactions, respectively. In their Fig. 4, Hu and coworkers⁸ showed that noble metals (e.g., Ag, Au, Pt) grow on TiO₂ in 3D island mode while alkali and other less noble metals (e.g., Na, Ba, Al) grow in 2D layer mode, and most transition metals are in a transition zone where both 3D or 2D growth could occur.

Consider the deposition of Ag on an oxide substrate a fraction f of which is covered with another metal M. The change of surface energy can be written as

$$\Delta\gamma = \gamma_{Ag} + \gamma_{Ag-substrate} - \gamma_{substrate} \quad (2)$$

with

$$\gamma_{Ag-substrate} = \gamma_{Ag-M}f + \gamma_{Ag-oxide}(1-f) \quad (3)$$

$$\gamma_{substrate} = \gamma_Mf + \gamma_{oxide}(1-f) \quad (4)$$

The interfacial energy at the boundary of metals and possible strain energies are neglected. To further evaluate these expressions containing the coverage f and the specifics of the seed material, we can approximate the change of surface energy by $\gamma_M \approx -\Delta H_{\text{sublimation of M}}$, describing the strength of the lateral metal-metal interactions, and $\gamma_{metal-substrate} \approx -\Delta H_{\text{oxide of metal}}$, describing the strength of the metal-oxide interactions. The change of surface energy is approximately

$$\Delta H = \left(-\Delta H_{\text{sublimation of Ag}} + \Delta H_{\text{oxide of Ag}}\right) - \left(-\Delta H_{\text{sublimation of M}} - \Delta H_{\text{Ag-M}} + \Delta H_{\text{oxide of Ag}}\right) f. \quad (5)$$

Since the heat of formation of the silver oxide is small, this expression can be further simplified to

$$\Delta H = -\Delta H_{\text{sublimation of Ag}} - \left(-\Delta H_{\text{sublimation of M}} - \Delta H_{\text{Ag-M}}\right) f, \quad (6)$$

which is an expression that can easily be evaluated using data from the literature^{9,10}; $\Delta H > 0$ implies island mode, and in the opposite case, $\Delta H \leq 0$, the films tends to grow in a layer. From eq.(6) one can find that (i) at very low seeding coverage, $f \rightarrow 0$, island growth occurs ($\Delta H > 0$ since $\Delta H_{\text{sublimation}}$ is negative); (ii) as f increases, ΔH is reduced and may become negative at a critical coverage f_c , (iii) as f further increase towards a coverage of a monolayer or more, one needs to consider the growth mode of the metal layer on its own right. Based on eq.(1) one can realize that in most cases the seed layer grows in islands because the surface free energy of metals is generally higher than the surface energy of an oxide. Therefore, for sub-monolayer coverage and for certain metals only, eq (6) predicts that $\Delta H \leq 0$, which gives layer growth of silver with earlier coalescence and reduced interface and surface roughness.

In summary, we have studied the effect of very small amounts of transition metal on the nucleation and coalescence of silver films. Onset of silver coalescence and surface roughness was found to be very sensitive to the kind and amount of seed material. Sub-monolayer amounts (nominally 0.1 nm) of most materials (especially pronounced with Nb and Ti) lead to significant smoothing and coalescence at thinner silver thickness. If more than the equivalent of a monolayer was deposited (0.2 nm and more), greater roughness and coalescence at greater thickness was observed. The observations can be explained in a thermodynamic model of surface energies where the enthalpy of formation of the metal and the heat of formation of the oxide are the decisive parameters.

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Figure Captions

FIG. 1 Sheet resistance of filtered arc deposited silver films on TiO_2 coated glass substrate. Very small amounts of Nb promote the onset of silver coalescence.

FIG. 2 AFM pictures ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of the silver surface deposited by filtered arc on TiO_2 coated glass without Nb (top), with nominal 0.1 nm Nb (center), and with nominal 0.2 nm Nb (bottom).

FIG. 3 Sheet resistance of silver films on ZnO:4at\%Al with sputtered Ti as the seeding layer material.

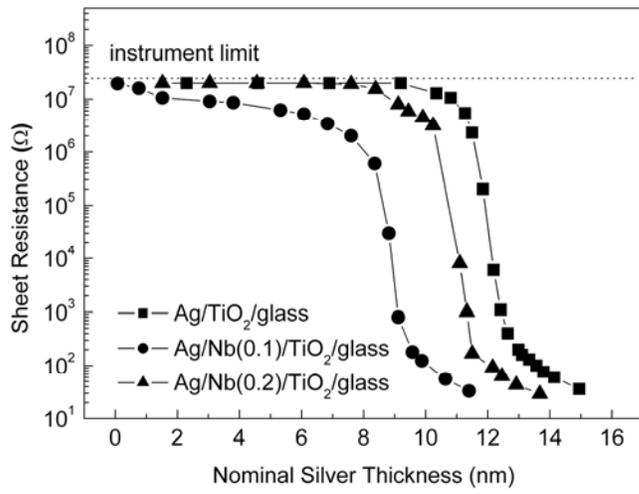


Fig. 1

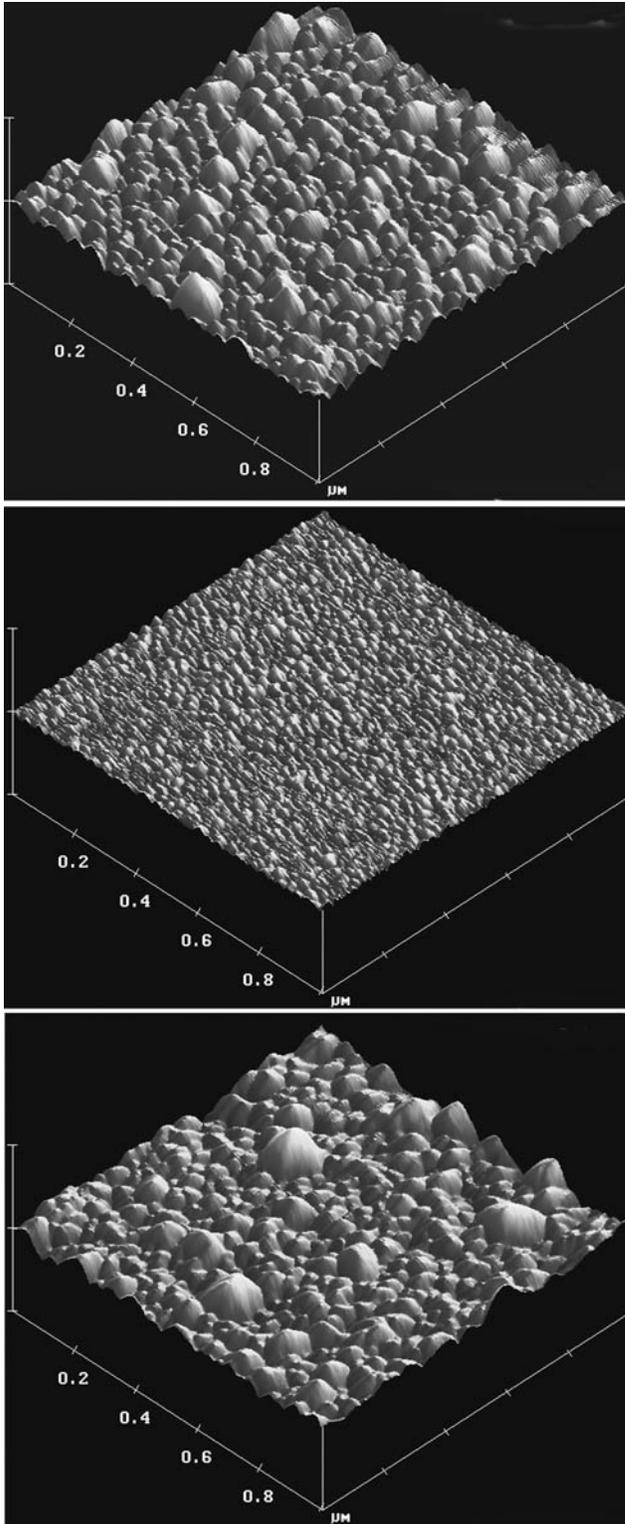


Fig. 2

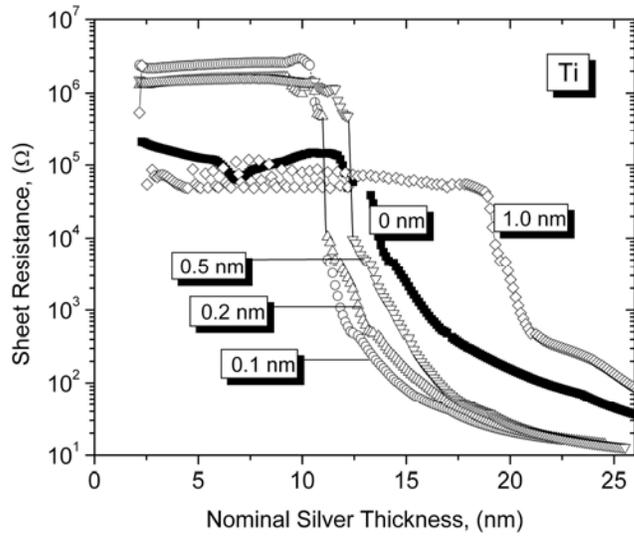


Fig. 3