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Evidence of germanium segregation in gold thin films

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ABSTRACT

Using X-ray Reflectometry (XRR) and X-ray Diffraction (XRD) measurements, we investigated the crystallinity of ~35 nm-thick gold films deposited on glass substrates with 2 nm-thick germanium wetting interlayer. Such wetting decreases the average grain size in the Au film and introduces gradient growth. With X-ray Photoelectron Spectroscopy (XPS) we measured the atomic concentration of Ge as a function of subsurface depth. Our results show the highest concentration of Ge atoms near the surface and the lowest at the Au/substrate interface, which is most likely the result of segregation. Ellipsometric measurements demonstrate that although presence of Ge atoms segregated in the system introduces additional plasmonic bands in the permittivity spectrum, the intensity of these bands is low in comparison to the intensity of the Drude term, which is greater than for the pure Au film. Annealing the Ge-wetted Au films immediately after the deposition decreases the value of the Dude term, however still not to the level of the nonwetted films, which suggests that some kind of mixing still occurs.

1. Introduction

Interest in two related phenomena: grain boundary diffusion and segregation dates back to studies on durable and low-loss interconnects in microelectronics. Deposition of gold on a silicon substrate with chromium as an adhesion interlayer resulted in the interdiffusion process through grain boundaries and adverse complete mixing of Au with Si at temperatures above 370 °C [1]. In another example, segregation of germanium atoms onto the surface of the growing silver layer was observed when Ag was deposited directly on Ge(111) substrate [2].

Grain boundary diffusion is a relocation of admixture atoms from the lattice points of the metal to the boundaries of nanocrystals, which results in a reduction of lattice strain energy. Surface segregation is a displacement of admixture atoms from all kinds of inhomogeneities in the polycrystalline metal matrix towards free surfaces, grain boundaries, interfaces between different phases as well as other low-coordination defects, which results in a reduction of Gibbs free energy of solute atoms [3,4]. Several models for grain boundary diffusion and admixture segregation were developed based on the estimation of either surface free energy of the constituents, enthalpy of mixing of the substances, or lattice strain energy values [5–9].

The distinction between the two effects is possible with measurements of the elemental composition of surfaces using Auger electron and X-ray photoelectron spectroscopy. The latter method, when combined with ion beam etching of sample surface, gives decisive quantitative concentration profiles for searched elements.

Nowadays, studies on grain boundary diffusion and segregation are motivated by the demand for low-loss plasmonic structures where long-range plasmons may propagate. To smooth the metal-dielectric interface and reduce scattering of surface plasmon-polariton (SPP) waves on metal-dielectric interfaces several wetting materials are used, such as nickel [10], niobium [11] chromium, titanium and their oxides [12–16]. However, due to high losses of the metals and not perfect adhesion of silver and gold to oxides, recently also carbon-based [17] and organic materials [18,19] are being used as wetting layers. In particular, Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [20] and 3-aminopropyl trimethoxysilane (APTMS) [21] are promising materials for silver and gold deposition, respectively. Influence of optimum evaporation conditions on the smoothness of silver films was also studied [22]. Another incentive is connected with wide studies on advanced functional materials with tailored electromagnetic properties [23–26].

A number of works have reported on ultra-thin germanium wetting films for smoothing silver thin films [27–29] and segregation of Ge atoms in silver [30–33]. Segregation phenomenon is driven by specific interactions of Ge and Ag as well as a unique crystallinity profile which

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is a result of enhanced wetting of Ag crystals to the substrate due to the presence of Ge atoms at the interface [33]. Since silver and gold are in the same group in the periodic table, they share many properties, out of which the most significant one regarding the possible wetting and segregation process is the same space group ($Fm\bar{3}m$) and almost identical lattice constant. This should translate into similar crystallinity in a thin film. Indeed, Lončarić et al. have shown, that for films of thickness below 12 nm, an island growth is observed for both silver [34] and gold [35,36], while in another work the authors investigate the promoted adhesion of gold to silicate substrates due to Ge wetting film [37].

In this work, we report on XRR, XRD, XPS, atomic force microscopy (AFM), ellipsometric and electrical measurements of 35 nm-thick gold films deposited on glass substrates with 2 nm-thick Ge interlayers. Since germanium has the same space group as gold, intense segregation is expected. The XRR and XRD measurements allowed do determine the nanocrystal size and density profile of the gold film, while with the XPS measurements the atomic concentration of germanium as a function of subsurface depth was determined. From ellipsometric measurements we have derived the effective optical parameters of the Ge-Au system.

2. Materials and methods

~2 nm-thick Ge films and 35 nm-thick Au films were deposited from fabmate or tungsten crucibles using PVD75 Lesker e-beam evaporator, on fused silica substrates with RMS roughness equal to 0.3 nm. The purity of the evaporation materials was 4 N for gold and 5 N for germanium Before evaporation, substrates were cleaned with argon flow at 2 bar pressure. Ge was evaporated at an average deposition rate of 0.5 Å/s. Gold films were evaporated at an average deposition rate of 2 Å/s. The deposition rate and total film thickness were monitored by two quartz weights inside the deposition chamber. Film thicknesses were verified by Dektak 6 M stylus profiler using a three-step process: first, a layer of each material was deposited until the quartz weight showed a thickness of ~200 nm. Then, the thickness was measured using Dektak 6 M stylus profiler. If the result diverged, the appropriate multiplicative parameter was entered into a calibration software (e.g. if the profiler showed 180 nm, then the software multiplied the reading of the quartz weight by 0.9). This procedure was then repeated to minimize the errors. Finally, the layers of the desired thickness were evaporated and verified by the profiler. The base pressure was 2×10^{-5} Torr in the vacuum chamber and did not exceed 5×10^{-5} Torr during the whole deposition process. The crucible-substrate distance was 40 cm.

To avoid corrosion, 3 N LiF was evaporated from a tungsten crucible at an average deposition rate of 1 Å/s to form a 3 nm-thick capping layer. We chose this material as a capping layer since it is easy to evaporate and, unlike SiO_2 or Al_2O_3 does not segregate into the metal structure, and therefore does not influence the segregation of germanium. Ellipsometric measurements of 3 nm LiF deposited on glass substrates revealed, that it can be treated as a continuous 3nm-thick layer with permittivity as provided in the literature [38]. The same is true for such film annealed at 300 °C, thus we may assume that little or no decomposition is occurring. This is in consistency with XPS measurements which reveal similar F surface concentration, with deviation not exceeding 6%.

AFM measurements were conducted on the day of the deposition, prior to LiF evaporation, using the Bruker Dimension Icon microscope working in the scan-assist mode at the solid-air interface. Cantilevers with spring constant k = 0.4 Nm^{-1} were used, the resonant frequency was in the range of 70–80 kHz. A typical image scan frequency was 1 Hz with a resolution of 512 × 512 px.

The X-ray Reflectometry measurements were performed 3 days after the deposition, using the Bruker Discover D8 X-ray diffractometer working with Cu Kα line source of wavelength 0.154 nm, the diffraction signal was recorded with point scintillation detector. The monochromatic parallel beam was formed by a crossed parabolic Goebel mirrors. The data analysis was based on finding the proper electron density profile for which with XRR generated data matched the experimental one. Data fitting was performed using Leptos 4.02 software package provided by Bruker. The electron density was simulated by 'box' type function. The thickness of the Ge wetting film was an adjustable parameter (but the density of this film was fixed) and for all Ge-wetted samples, the fit equated 2 ± 0.5 nm. The optical thickness of the Au layer was fitted for the sample without the Ge wetting film, and then fixed for all other samples, while its density was left as a fittable parameter for all samples. The thickness and density of the LiF protective film were fitted for the sample without Ge wetting film, and then fixed for all other samples. The Ge/Au and Au/LiF interface roughness were left as fittable parameters. More information about XRR modeling can be found in [39] and references therein.

The wide-angle X-ray diffraction (XRD) measurements were performed in transmission mode using Bruker Discover D8 GADDS system. The system works with Cu Kα X-ray source. The X-ray patterns are recorded with 2D Vantec 2000 detector. For precise diffraction angle measurements, also Bruker Discover D8 system was used, but the measurements were performed in reflection geometry in $\theta - 2\theta$ mode. The diffracted beam intensity was recorded with the 1D Vantec-1 detector. The width and position of the signals were analyzed with TOPAS software. The average size of the gold grains was calculated by fitting the Gaussian profile to the dominant diffraction peak at 38.2° which corresponds to 111 crystallographic direction, all other diffraction peaks in the XRD spectrum were extremely weak due to the alignment of crystallites. The Full Width at Half Maximum (FWHM) parameter of the fitted Gaussian profile was used in the Deby'e-Scherer formula:

$$d = \frac{0.89\lambda}{FWHM \cdot \cos\theta} \tag{1}$$

where d is the average grain size, λ is the incident wavelength (in this case 0.154 nm) and θ is the Bragg diffraction angle. The lattice constant was then derived from the position of the fitted Gaussian profile.

Ellipsometric azimuths Ψ and Δ of fabricated samples were measured 10 days after the deposition in the UV-VIS-MIR spectral range (0.06–6.5 eV) for three angles of incidence (65°, 70° and 75°) by the use of two instruments: V-VASE (J.A.Woollam Co., Inc.) in the UV-VIS-NIR and Sendira (Sentech GmbH) in the MIR. The complex dielectric functions of effective Ag layers with segregated Ge atoms were extracted using a layered model of the samples. The permittivities were then interpreted in terms of the Lorentz, Drude-Lorentz and modified Lorentz [40] oscillator models. The optical thickness of the samples was left as a fittable parameter in the model which allowed to confirm that the thickness of the gold samples does not exceed 35 nm. In fact, the best fit is achieved for slightly lower thicknesses of 30 ± 1 nm.

The XPS data was obtained 10 days after deposition by using VG-Scienta R3000 analyzer and standard Al Kα X-ray radiation source (1486.6 eV). Photoelectrons were collected from the surface at normal angle, the X-ray radiation angle was 55° with respect to the normal of the sample. In order to obtain the information about chemical composition of subsurface layers, samples were sputtered with Ar^+ ion beam. The sputtering interval between recording the data was 2 min. The surface of each sample was bombarded at the angle of 69° by 4 keV ions. During the sputtering ion beam scanned 4 × 4 mm area of the surface in order to assure even etching. Atomic concentrations of detected elements were estimated by fitting experimental data to the Gauss-Lorentz shapes by means of CasaXPS® software. All XPS measurements were performed in UHV system at the base pressure $\leq 2 \cdot 10^{-10}$ mbar. The broadening and shifting of the Ge2p peak are observed in all the samples as an effect of ion sputtering (see Fig. S1 in supporting information).

All samples remained in ambient air for ten days since the deposition of layers. Therefore, there is a relatively big concentration of surface contaminants. In XPS spectra these contaminants are represented by distinct peaks of O1s and C1s. The concentration of oxygen and

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