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Growth of Ultrasmooth Silver Thin Films Deposited with a Germanium Nucleation Layer

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Ultrasmooth Ag Introduction

Silver (Ag) thin films have been the most frequently employed material for innovative applications in a wide range of fields including nanoplasmonics, solar energy, optical waveguides, OLEDs, and superlenses. The conventional methods of depositing Ag thin films on insulators by e-beam evaporation, chemical vapor deposition, ion-beam sputtering, rf/dc sputtering, electroless plating, and pulsed laser deposition tend to proceed in Volmer-Weber growth mode, which often results in rough Ag surface morphologies. Such rough surface morphology combined with large grain size leads to a significant loss that severely lowers the performance and yield of, for instance, plasmonic devices and metamaterials. The structural properties of optically thin (15 nm) Ag films deposited on SiO₂/Si(100) substrates with a germanium (Ge) nucleation layer were studied. The surface roughness of Ag thin films was found to decrease significantly by inserting a Ge nucleation layer with a thickness in the range of 1 to 2 nm (i.e., smoothing mode). However, as the Ge nucleation layer thickness increased beyond 2 nm, the surface roughness increased (roughing mode).

Experiment

Si(100) covered with a ~3 nm native oxide (SiO₂) layer was used as the substrate. The SiO₂/Si substrates were treated in a cleaning bath of H₂SO₄/H₂O₂ (3:1), rinsed with deionized water, and dried with nitrogen (N₂). Subsequently, Ge and Ag were sequentially deposited onto the substrates, without breaking vacuum, in an electron-beam evaporation system (CHA Mark 50 ISS). The evaporation chamber was held at a base pressure of ~1 μTorr and ambient temperature during the deposition. The deposition rates of Ge and Ag were 0.01 and 0.1 nm/s, respectively. The thickness of Ge was varied (0, 1, 2, 5, and 15 nm) while the thickness of Ag was fixed at 15 nm. The morphological and crystallographical characteristics of Ag thin films with different Ge nucleation layer thicknesses were assessed by cross-sectional transmission electron microscopy (XTEM), reflection high-energy electron diffraction (RHEED), X-ray diffractometry (XRD), grazing incidence X-ray diffractometry (GIXRD), X-ray reflection (XRR), and Fourier transform infrared spectroscopy (FTIR).

XTEM and RHEED

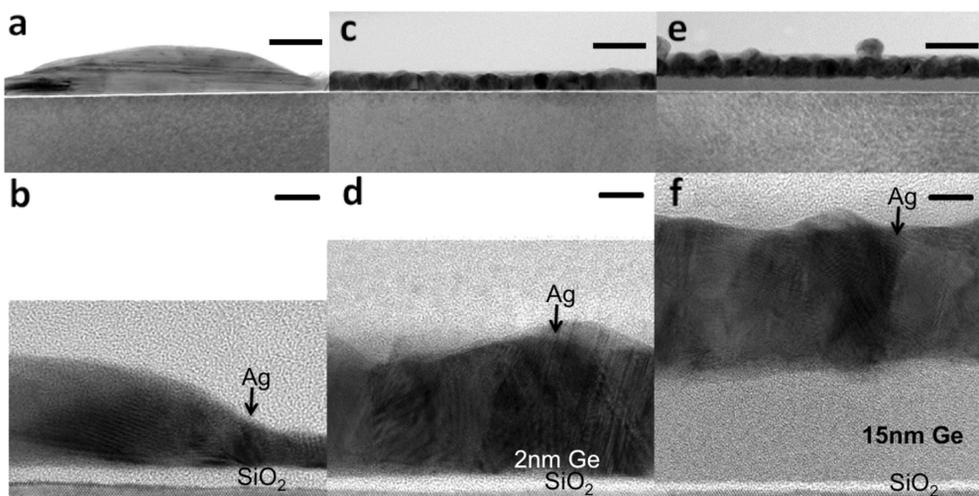


Figure 1. XTEM images of Ag/Ge/SiO₂/Si for various thicknesses of Ge at two different magnification settings: (a, b) with no Ge nucleation layer, (c, d) with a 2 nm Ge nucleation layer, and (e, f) with a 15 nm Ge nucleation layer. The scale bar for (a, c, e) is 50 nm and for (b, d, f) is 5 nm.

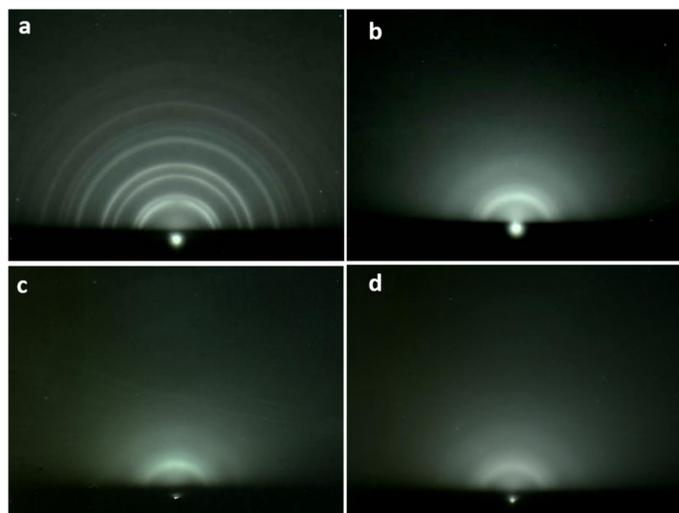


Figure 2. RHEED patterns of Ag/Ge/SiO₂/Si stacks for near-optimal Ge thickness: (a) with 0 nm Ge, (b) with 0.5 nm Ge, (c) with 1 nm Ge, and (d) with 2 nm Ge. The RHEED pattern of a sample without a Ge layer shows many distinct Laue rings, indicative of a polycrystalline Ag surface. As the thickness of Ge progresses from 0.5 to 1 to 2 nm, the rings became more diffuse, which is evidence of a smoother Ag surface.

X-Ray Summary

Table 1. FWHM and corresponding average crystallite sizes from XRD and relative intensity of the peaks associated with each lattice plane from GIXRD for the five samples

samples	XRD		GIXRD				
	FWHM (degree)	crystallite size (nm)	111 (38.2°)	200 (44.3°)	220 (64.3°)	311 (77.6°)	222 (82.2°)
1.15 nm Ag/SiO ₂ /Si	0.365	27.7	100	40	25	26	0
2.15 nm Ag/1 nm Ge/SiO ₂ /Si	0.719	14.0	100	0	65.4	16.5	0
3.15 nm Ag/2 nm Ge/SiO ₂ /Si	0.933	10.7	100	13	32	13.2	0
4.15 nm Ag/5 nm Ge/SiO ₂ /Si	0.747	13.5	100	26.8	31.3	17.6	2.9
5.15 nm Ag/15 nm Ge/SiO ₂ /Si	0.603	16.7	100	18.8	13.6	12.8	2.2

XRD, GIXRD, and XRR

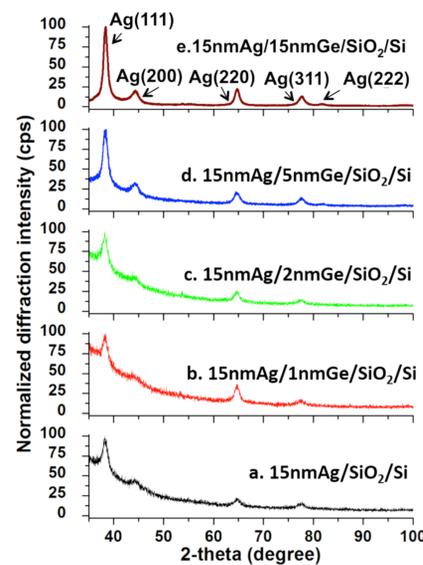


Figure 3. Grazing incidence X-ray diffraction (GIXRD) of five Ag/Ge/SiO₂/Si samples with different Ge thicknesses. The total intensity (i.e., the sum of the four peak intensities) decreases and reaches a minima as dGe thickness increases from 0 to 2 nm, suggesting that the polycrystalline Ag film with dGe = 0 nm becomes quasi-amorphous with dGe = 2 nm.

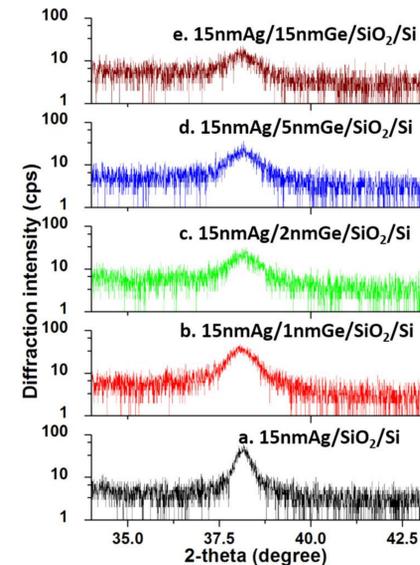


Figure 4. X-ray diffraction (XRD) of five Ag/Ge/SiO₂/Si samples with different Ge thicknesses. The sample without the Ge layer has the smallest FWHM of the Ag(111) peak at 38.2°, indicating the largest crystallite size in these five samples. The samples with a thin Ge layer (1–5 nm) exhibit broad Ag(111) peaks manifesting in the Ag film containing smaller grains. With thicker Ge layers (5–15 nm), the crystallite sizes increased again, leading to a rougher Ag surface.

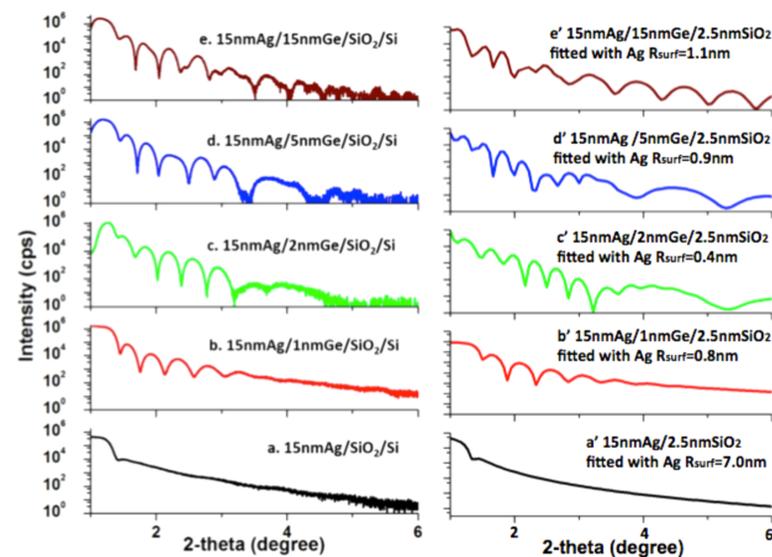


Figure 5. X-ray reflection (XRR) of five Ag/Ge/SiO₂/Si samples with different Ge thicknesses (left). The XRR spectrum of the sample without a Ge layer exhibits a damped oscillation amplitude, indicating the presence of a rough surface. For samples with 1 and 2 nm Ge layers, the oscillations in the reflected X-ray intensity show rather persistent and consistent oscillation in reciprocal space, indicating the presence of much smoother surfaces. With an increased Ge thickness to 5 nm and then 15 nm, the oscillation becomes less persistent, suggesting that the surface roughness increases with a Ge layer thicker than 2 nm. The experimental XRR profiles were fitted by varying the thickness and interfacial roughness for the Ag/Ge/SiO₂ stacks by employing a genetic algorithm model. The obtained R_{surf} of Ag surfaces with different Ge thicknesses are shown (right).

FTIR of SAMs

Self-assembled monolayers (SAMs) of CH₃-terminated alkanethiolate (CH₃-(CH₂)₁₇-SH) were formed by immersion in an ethanol solution containing the alkanethiolate (molar concentration of 0.01 M) for extended times (>24 h) at room temperature to obtain a strong hydrophobic surface on Ag thin films deposited with and without a 2 nm Ge nucleation layer.

FTIR spectra provide indirect but highly relevant proof of the smoothing role of a 2 nm Ge nucleation layer. The sample with a 2 nm Ge layer resulted in stronger absorbance at all four peaks and a narrower a-CH₂ peak, suggestive of a more orderly arrangement of alkanethiolate complexes, which was presumably caused by a smoother Ag surface established on the 2 nm Ge layer.

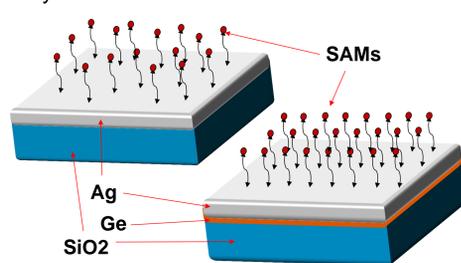


Figure 6. Illustration of (left) SAMs disorderly adhering to Ag/SiO₂ surface and (right) SAMs with greater order and alignment on Ag/Ge/SiO₂ surface. Illustrations (not drawn to scale) represent the assumption that smooth Ag on Ge wetting layer allows SAMs to adhere more orderly and yield stronger FTIR vibrational mode signals.

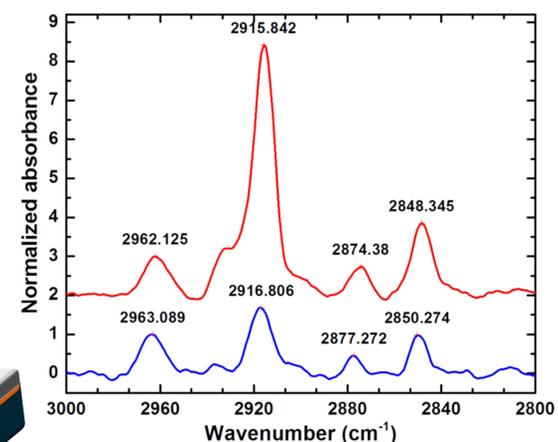


Figure 7. FTIR of two silver thin film samples with an alkanethiolate SAM coating. The blue plot shows SAM/Ag/SiO₂ absorbance, and the red plot shows SAM/Ag/2 nm Ge/SiO₂ absorbance. In both cases, the Ag nominal thickness was 15 nm. The stronger absorbances and narrower a-CH₂ peak at 2916.806 cm⁻¹ show a more ordered arrangement of alkanethiolate complexes, indicative of a less rough surface in the sample with a 2 nm Ge layer.