Single-Crystalline Silver Films for Plasmonics

Jong Hyuk Park, Palak Ambwani, Michael Manno, Nathan C. Lindquist, Prashant Nagpal, Sang-Hyun Oh, Chris Leighton, and David J. Norris*

Surface plasmon polaritons (SPPs) are hybrid photon-electron waves that propagate along a metal-dielectric interface.[31] Due to their hybrid nature, SPPs can be exploited to control and concentrate light below the optical diffraction limit, generating large electric fields in confined regions.[32–34] This unique characteristic of SPPs has led to their application in many areas including surface-enhanced spectroscopy,[35–37] molecular sensing,[38–40] nanofocusing,[41–43] subwavelength waveguides,[44,45] optical antennas,[46,47] data storage,[48,49] and photovoltaics.[50] In many cases, patterned metals are employed to generate and manipulate SPPs. The precision of these structures and the dielectric properties of the metal are critical factors in determining the performance of plasmonic devices.[1,2] Surface inhomogeneities should be minimized to avoid SPP scattering during propagation, and the metal should have high conductivity and low optical absorption to enhance optical confinement and reduce losses.

To obtain patterned metallic films, a two-step procedure is typically utilized. Metals are first deposited via evaporation or sputtering on a substrate and then patterned with focused-ion-beam (FIB) milling.[21,22] However, since the deposited films are polycrystalline and etch rates vary for different grain orientations,[23] the patterning procedure can lead to increased surface roughness. One possible solution is to prepare single-crystalline metals, which will etch more uniformly and lead to precise patterns. To address this possibility, single-crystalline silver and gold samples have been prepared by several approaches, including the Czochralski process,[24] colloidal chemistry,[25–29] and nanofocusing.[30] The resulting samples have demonstrated great promise for plasmonics. However, they also have disadvantages. The Czochralski process requires specialized equipment and additional polishing to obtain smooth surfaces, leading to high costs. Colloidal chemistry leads to micrometer-scale flakes or nanowires that are dispersed in a solvent. Consequently, they are susceptible to aggregation, are inhomogeneous in size and shape, and are inconvenient to place and manipulate for device fabrication. It would be preferable to have a simple approach to produce continuous, smooth, and inexpensive single-crystalline metallic films, which could then be used as the starting material for a variety of plasmonic devices.

Herein, we demonstrate that epitaxial growth can provide an effective route to obtain smooth single-crystalline metallic films for plasmonics.[31–35] In epitaxy, the crystalline structure and orientation of the growing films are strongly influenced by those of the underlying substrate. Compared to single-crystalline films obtained via the Czochralski process or colloidal chemistry, epitaxial metallic films can provide many advantages: a flat surface over a large area, an accurately controlled thickness, and high crystallinity. Epitaxial growth is also a simple and reproducible process that offers lower cost. Finally, it is applicable to both silver and gold, which are the most widely studied metals for plasmonic applications.

In this work, we focus on silver because it has better optical properties at visible wavelengths at less expense. For the substrate, several reasonably well lattice-matched materials such as mica, MgO, Al2O3, and silicon have already been used for epitaxial growth of silver films.[32-35] We chose mica due to its flat surface, high chemical stability, low cost, and propensity for smooth epitaxial growth of Ag and Au. We deposited nominally 100-nm-thick silver films epitaxially on mica substrates by dc magnetron sputtering under controlled conditions. It is known that the surface morphology and crystalline structure of such epitaxial films are strongly influenced by the deposition rate and substrate temperature.[31–33] Since a high deposition rate is needed to make the surface continuous and flat,[33] i.e., to avoid surface-diffusion-enabled agglomeration, we utilized the maximum deposition rate (1.65 nm/s) that was achievable via simple means in our sputtering system. As expected, a high substrate temperature of over 300 °C was necessary to form a single-crystalline structure. Table 1 reports the deposition conditions for our samples. The film (denoted SCI) deposited with a substrate temperature of 350 °C was particularly smooth over large areas, as detailed further below.

The microstructure of our films was characterized via high-resolution wide-angle X-ray diffraction (XRD). Figure 1a shows that the wide-angle XRD pattern of SCI contains only the Ag(111) and Ag(222) peaks in addition to those from the substrate. This indicates that the film is single crystalline in the z (growth) direction and aligned (111) out-of-plane. This is expected from prior work on Ag grown on c-axis mica,[33] as well as simple lattice-matching models. The rocking curve through
the Ag(111) peak has a full-width-at-half-maximum (FWHM) of 0.3°, indicative of a low mosaic spread in the film (Figure 1b). A grazing-incidence in-plane X-ray scan was also performed on the Ag(220) peak and it showed the 6-fold symmetry expected for (111) oriented films (Figure 1c). These results demonstrate that SC1 is also single crystalline in plane. Furthermore, Figure 1d shows the grazing-incidence X-ray reflectivity of SC1. Simulations suggest Ag surface roughness of 0.7 nm over the long lateral length scale probed. When the film thickness was increased up to 200 nm under the same growth conditions (film SC2 in Table 1), single crystallinity was maintained (see Figures S1 and S2 in the Supporting Information).

The surface morphology of our films was further quantified with atomic force microscopy (AFM). The surface of SC1 was continuous without pinholes or islands, and no grain boundaries were found (Figure 2a). The contrast observed in the AFM image of SC1 is due to mild height variations arising from the epitaxial growth mechanism. The root mean square (RMS) roughness was 0.82 nm measured over 2.5 × 2.5 μm², very close to the 0.7 nm extracted from X-ray reflectivity in Figure 1d. For the thicker sample grown under the same conditions (SC2), the surface was still continuous without any grain boundaries, with only a small increase in surface roughness (see Table 1 and Figure 2b).

Since flat single-crystalline films can result in reduced SPP propagation losses, these films should exhibit good performance for plasmonic applications. To demonstrate this, we compared our single-crystalline films with polycrystalline films with identical surface roughness. Because it is difficult to obtain extremely flat surfaces with a roughness of less than 1 nm through conventional evaporation, the template-stripping method was used. 200-nm-thick silver films were deposited on clean silicon wafers and then stripped from the substrates using an epoxy backing layer. The roughness of the stripped surfaces was controlled by the deposition and stripping conditions. These template-stripped films showed Debye ring XRD patterns with a two-dimensional (2D) area detector (see Figure S3 in the Supporting Information), implying a randomly oriented polycrystalline grain structure. The conditions were also adjusted so that these films had nearly identical surface roughness (Figure 2c,d) as the epitaxial films, SC1 and SC2. The polycrystalline films with a roughness of 0.81 and 1.39 nm are denoted PC1 and PC2, respectively.

Using a multi-angle spectroscopic ellipsometer, we compared the dielectric functions of the single-crystalline and polycrystalline films. The epitaxial films exhibited dielectric functions with a larger negative real component (ε₁) and a smaller

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**Table 1.** Surface roughness and microstructure of sputtered Ag films as a function of deposition temperature. The pressure in the sputtering chamber was maintained at 6 mTorr with argon during deposition. RMS roughness was determined from AFM scans over an area of 2.5 × 2.5 μm².

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**Figure 1.** Structural characterization of a 97-nm-thick c-axis mica/Ag(111) film (SC1) deposited at 350 °C. (a) High-resolution specular X-ray diffraction (θ–2θ) scan with asterisk symbols indicating substrate diffraction peaks. (b) Transverse scan (rocking curve) through the Ag(111) diffraction peak. The measured transverse scan and a fitted Gaussian profile are represented by black dots and a solid red line, respectively. (c) Grazing-incidence in-plane X-ray diffraction scan (θ–scan) of the Ag(220) plane. (d) Measured (black circles) and simulated (solid red line) grazing-incidence specular X-ray reflectivity. The Ag surface roughness and thickness, extracted from the fit, are shown.

**Figure 2.** AFM images of single-crystalline Ag films [(a) SC1 and (b) SC2] and polycrystalline Ag films [(c) PC1 and (d) PC2]. These films have RMS roughness of 0.82, 1.30, 0.81, and 1.39 nm, respectively. All scanned areas are 2.5 × 2.5 μm².
imaginary component ($\varepsilon_2$) than the polycrystalline films, as shown in Figure 3. The larger negative $\varepsilon_1$ indicates higher conductivity. Indeed, the dc electrical resistivity of SC2 was measured to be less than that of PC2 (see Table S1 in the Supporting Information). The smaller $\varepsilon_2$ in the epitaxial films indicates a lower energy loss, which is important to enhance the propagation length of SPPs. Furthermore, the dielectric functions of the films were also affected by surface roughness. Even though this effect was not significant in the tested films due to a small difference in the surface roughness, films with smoother surfaces showed higher conductivity and lower optical absorption, consistent with previous work.\[40\]

To demonstrate the improved plasmonic properties of single-crystalline films over polycrystalline films, we measured the SPP propagation length in both types of films. Figure 4a shows a schematic of the experimental setup for the measurement.\[41\] A series of identical slits were patterned on both epitaxial and polycrystalline silver films via FIB milling. Then, a parallel groove was added adjacent to each slit at a distance, $d$. The slits and grooves were each 200 nm wide and 40 $\mu$m long, and $d$ was varied from 10 to 40 $\mu$m. When the sample was illuminated with white light from the substrate side, transmitted light through the slit generated SPPs that propagated along the silver surfaces. When these SPPs struck the adjacent groove, they were partially scattered into the far field and the resulting light was collected with an optical microscope. We measured the spectrum of the scattered light for all slit-groove pairs, and by fitting this to an exponential decay of intensity versus distance $d$, we extracted the propagation length of the SPPs as a function of optical wavelength.\[38\]

For each film, we determined two sets of values. To obtain the first set, we assumed that all of the SPPs propagated along the shortest path between the slit and groove (the dashed red arrow in Figure 4a). The results are plotted in Figure S4 in the Supporting Information. However, this approach underestimates the propagation length.\[22,38\] Some SPPs will be launched from the slit at an angle $\alpha$ (see Figure 4a) and yet still strike the groove. Thus, at short slit-groove separations, more SPPs will be scattered and detected. Due to the fixed length of the slits and grooves (40 $\mu$m), the range of angles $\alpha$ that will be collected decreases as the slit-groove separation increases. This causes an additional decay of the signal with $d$, which is purely geometrical, and leads to an underestimation of the SPP propagation length. Our second set of values is corrected for this effect. By assuming that the SPPs can be launched from the slit with equal probability at any angle $\alpha$, a geometrical factor that accounts for the average acceptance angle of each slit-groove pair was included in the model (see the Supporting Information for details). The resulting SPP propagation lengths for single-crystalline and polycrystalline films are shown in Figure 4b (SC1 and PC1) and 4c (SC2 and PC2).

We observe that SPPs propagate further on epitaxial films, which lack grain boundaries. With similar surface roughness, SC1 exhibited on average a $\sim$70% improvement in the SPP propagation length over PC1 (Figure 4b). The propagation length with SC2 increased on average $\sim$55% compared to PC2 (Figure 4c). This shows that the effect of the grain boundaries on the propagation length is critical for smooth surfaces. On rougher surfaces, SPP scattering by the surface roughness dominates. For this reason, compared to a polycrystalline film, the smoother epitaxial film (SC1) exhibited a larger relative improvement in the propagation length than the rougher one (SC2). Also, as previously reported,\[1,38\] smooth films (SC1 and
PC1) have longer SPP propagation lengths than rough films (SC2 and PC2).

Assuming that the surface has zero roughness and the SPPs are damped only by ohmic losses, we can estimate the theoretical propagation lengths using the measured dielectric functions from the same films. As shown in Figure 4b,c, the theoretical values of the propagation lengths are slightly larger than the actual SPP propagation lengths. If the roughness is incorporated into the theory, the theoretical curves decrease by ~5% and ~10% for SC1 and SC2, respectively. In addition, subtle surface contamination or oxidation, which is not included in the model, could lead to a decrease in the experimental curves.

Because we have measured the propagation lengths on both single-crystalline and polycrystalline films of the same roughness, we can in principle estimate the contribution of grain boundary scattering to the overall SPP propagation length. This contribution can be quantified in terms of a grain boundary scattering length, \( L_{gb} \). This is the length that SPPs would propagate if no other loss mechanisms were active. It was previously reported for gold films, where the scattering coefficient was determined to be 0.2%. If we estimate \( L_{gb} \) using films SC1 and PC1 (with \( g \sim 180 \) nm), we obtain an average \( L_{gb} \) of 120 \( \mu m \) with \( S_{gb} \) of ~0.15%. Similarly, SC2 and PC2 (with \( g \sim 140 \) nm) yield an average \( L_{gb} \) of 80 \( \mu m \) with \( S_{gb} \) of ~0.18%. However, these values must be considered as rough estimates, as discussed further in the Supporting Information.

Another important advantage of single-crystalline samples is that they are well suited to precise patterning. Figure 5 shows scanning electron microscopy (SEM) images of nanostructures fabricated in SC1 and PC1 patterned via FIB milling. A significant difference in the surface morphology of the nanostructures is observed (Figure 5a,c, and 5b,d, respectively). Even though both films had nearly identical surface roughness before patterning, the obtained structures on PC1 were very rough while precise nanostructures could be obtained for SC1. Since epitaxial films have a highly-oriented, single-crystalline structure, the entire surface has essentially the same etching rate during FIB milling. Therefore, the milling depth of the patterned areas is almost identical across the surface, and the increase in surface roughness is limited. On the other hand, different etching rates of the randomly oriented grains in the polycrystalline films cause a variation in the milling depth across the patterned areas and, thus, a deterioration of the desired pattern.

To quantify this difference, we patterned \( 10 \times 10 \) \( \mu m^2 \) squares of different depths on both single-crystalline and polycrystalline films via FIB milling. The surface roughness of each square was then observed via AFM. As expected, for the same FIB milling conditions, the squares on SC1 and PC1 showed different surface morphologies. The squares on SC1 exhibited a more uniform surface (Figure 6a), compared to the squares on PC1 (Figure 6b). Figure 6c shows the measured RMS surface roughness as a function of the milling depth. Before patterning, both epitaxial (SC1) and polycrystalline (PC1) films had nearly identical surface roughness. With increasing milling depth, the surface roughness of the patterned area on both films increased. However, for the epitaxial film (SC1), the increase in roughness saturated at a depth of 60 nm, while the roughness of the polycrystalline film (PC1) continued to increase. As a result, when the milling depth is 60 nm or deeper, the roughness of the
patterned area on PC1 is over three times larger than that on SC1. This shows that epitaxial films can provide more precisely patterned nanostructures as compared to the polycrystalline films. Such fine control is essential for accurate manipulation of SPPs with plasmonic devices.[28,39]

Thus, we have demonstrated that epitaxially grown silver films can provide several key benefits for plasmonics. Using a standard dc magnetron sputtering system, single-crystalline films can be easily obtained that are extremely flat over large areas. Because this flatness occurs on both sides, these films can be useful for devices that utilize long-range plasmonic waveguides[44] or extraordinary optical transmission.[2] The metallic films also exhibit an improved dielectric function with higher conductivity and lower optical absorption compared to polycrystalline films. This can lead to an increase in the SPP propagation length. Furthermore, when the epitaxial films are patterned via FIB milling, precise single-crystalline nanostructures can be obtained. The resulting films can therefore allow the fabrication of plasmonic devices with enhanced performance.

**Experimental Section**

Detailed experimental methods are provided in the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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[42] In practice, extracting $L_p$ is complicated by the discrepancy between experiment and theory, as well as the fact that the crystallinity also affects the dielectric functions. See Supporting Information for details.