Intrinsic Optical Properties and Enhanced Plasmonic Response of Epitaxial Silver

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Loss represents the most serious challenge that impedes progress and broad impact towards practical technology in the field of plasmonics.[1–3] Silver (Ag) is by far the preferred plasmonic material at optical frequencies due to its lowest loss among all metals. However, large discrepancies exist among widely quoted values of optical permittivity in Ag due to variations in sample preparation. A natural question arises: what are the intrinsic fundamental optical properties of Ag? Using atomically smooth epitaxial Ag films, we extracted new optical permittivity highlighting significant loss reduction in the visible frequency range. We measured a largely enhanced propagation distance of surface plasmon polaritons (SPPs), which confirmed that the intrinsic loss in Ag is lower than previously considered possible. The new optical constants are free of extrinsic spectral features typically associated with grain boundaries and localized plasmons inevitably present in thermally deposited films.

Plasmonic devices are typically operated in the Drude regime below the transition threshold, where the Ohmic loss is determined by the electron scattering rate due to electron-electron, electron-phonon, and impurity/defect scattering processes. Loss is concisely captured by the imaginary part of the permittivity ($\varepsilon_i = \varepsilon_\text{e} + i\varepsilon_\text{c}$). In this paper, we carefully examine the optical constants of Ag for several reasons. First, the two most cited sets of Ag optical constants, from papers by Johnson/Christy (JC)\(^4\) and Palik,\(^5\) report imaginary parts of permittivity that differ by more than a factor of 3 at visible wavelengths, likely due to different sample preparation procedures. This discrepancy can lead to unreliable predictions of new plasmonic devices and metamaterials, especially those dependent on nonlinear processes. Second, the JC measurements conducted more than four decades ago still represent the lowest loss reported to date for Ag, and thus have been widely used to design and model plasmonic devices and metamaterials. However, there are spectral features in the optical permittivity reported by JC likely only associated with thermally deposited film, thus not intrinsic to Ag. Finally, single crystalline or epitaxial Ag has recently emerged as a promising material platform for plasmonic applications as notably demonstrated by the ultralow threshold nanolaser.\(^6\) Therefore, it has become of utmost importance to determine the ultimate limit in the performance of Ag as a plasmonic material platform. This goal can be accomplished by measuring the intrinsic optical properties of epitaxial Ag films of the highest quality.

In this work, we performed careful spectroscopic ellipsometry (SE) measurements and analyses on atomically smooth, epitaxially grown, single crystalline Ag films,\(^7–10\) and accurately extracted Kramers-Kronig (K-K) consistent optical constants. Our measurements suggest that the intrinsic loss in Ag is significantly lower, by up to a factor of 2 in the visible wavelength range, than the best values previously reported by JC.\(^4\) We also measured SPP propagation distances along these epitaxial Ag films, finding greatly enhanced propagation lengths, approaching the fundamental limit determined by the new optical constants at both visible and near-infrared (NIR) frequencies. The measured propagation distance confirms that the loss determined from the permittivity data reported by JC is not an intrinsic limit. Finally, simulations for a dolmen Fano metamaterial and a plasmonic nano-laser using these new optical constants demonstrate that these results will have wide implications for metamaterials and other plasmonic applications.\(^11–13\)

Atomically smooth Ag films were grown using molecular beam epitaxy (MBE) on heavily doped Si(111)-7 × 7 substrates (see Supporting Information S0 for growth detail). The high surface quality of a 45 nm oxide capped epitaxial film was confirmed by atomic force microscopy (AFM) shown in Figure 1a. For comparison, a 50 nm thermally deposited film was also scanned, as shown in Figure 1b. The evaporated film has a root mean square (RMS) roughness of 3.27 nm while the epitaxially grown film has a roughness of only 0.36 nm, nearly an order of magnitude smaller. We note that an AFM scan of an uncapped epitaxial film showed the same the surface topology characteristics and similar RMS values of roughness (data not shown). Low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) patterns shown in

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We performed SE measurements and analyses, to multiple epitaxial and thermal silver films (see Supporting Information S1-S4 for complete details). We present here results from three representative films: an uncapped 40 nm epitaxially grown film, a 45 nm epitaxial film capped with 1.5 nm of MgO and 2 nm of Al₂O₃, and an uncapped 50 nm thermal film deposited at a rate of 0.35 nm/s serving as control. The MgO/Al₂O₃ cap is a crucial element to prevent the rapid degradation of epitaxial silver due to surface oxidation in ambient conditions, and we confirmed via SE measurements that the Ag film’s pristine quality persists even after capping. In our fitting, we used simple Ag/Si or capping/Ag/Si structural models for the epitaxial films as shown in Figure 1e. The fitted result for ε₂ from each film is plotted against those for a 40 nm thermally deposited film measured by JC and the data compiled by Palik from Palik’s Handbook of optical constants. The vertical dashed lines in (f-h) indicate the energy at which ε₂ for the epitaxial Ag is ∼2 times smaller than that of the JC measurements. The light gray shaded curve represents the errors in the JC data, as originally quoted by the authors.

Figure 1c and 1d, respectively, taken in-situ, further confirm the long-range single crystalline nature of these films.

Figure 1. AFM scans of (a) a 45 nm epitaxial (2 nm Al₂O₃/1.5 nm MgO capped) and (b) a 50 nm thermally deposited (0.03 nm/s deposition rate) Ag film. (c) LEED and (d) RHEED patterns of an epitaxially grown Ag film. (e) Layered structures of our Ag film samples with and without oxide capping. Energy dependence of ε₂ extracted from SE measurements on (f) an uncapped 40 nm epitaxial film, (g) a 45 nm epitaxial film capped with 1.5 nm of MgO and 2 nm of Al₂O₃, and (h) an uncapped 50 nm thermal film deposited at a rate of 0.35 nm/s. Each film is plotted against data taken by JC and from Palik’s Handbook of optical constants. The vertical dashed lines in (f-h) indicate the energy at which ε₂ for the epitaxial Ag is ∼2 times smaller than that of the JC measurements. The light gray shaded curve represents the errors in the JC data, as originally quoted by the authors.
lower loss than JC’s values in the 1.8–2.5 eV range, while the control film shows values in between JC and Palik data. The residues in this region are small and centered around zero for all films, suggesting that our model fits the data very well. In the lowest energy range below 1.5 eV, the error becomes large due to reduced detector efficiency and our extracted ε₂ appears to be larger than that reported by JC. We note that the original JC data contain large errors in this same energy region (gray shadow in the Figure 1f–1h). Thus our measurements are consistent with JC’s in this lowest energy region.

The residues shown in Figure 1f–1h are not completely random: on close inspection, in the energy range near 3.7 eV, indicated by the orange circle in all panels, one can see a sizable peak in the residue for the thermal film (Figure 1h) that is absent in both epitaxial films (Figure 1f and 1g). We suggest that this peak is associated with the presence of grain boundaries. The same feature around the same energy level is present in the JC data. Previous theoretical studies modeling the effect of grain boundaries have suggested that they lead to higher loss in a certain wavelength range determined by the average size.[18] These earlier calculations have, in fact, predicted higher loss in this energy range.

Our measured optical constants suggest improved theoretical limits to the performance of plasmonic devices. In order to experimentally demonstrate these improvements, we measured SPP propagation distances over the 45 nm epitaxial Ag film. We excited and detected the SPPs in reflection geometry, as illustrated in Figure 2a. Light incident from an oblique angle on a single groove launches the SPPs, which are subsequently detected at a series of output coupling slits with increasing distance from the launching site, as shown in the scanning electron microscope (SEM) image in Figure 2b. We used two different incident wavelengths (632 nm and 880 nm). The integrated optical signals from the output grooves are plotted as a function of propagation length in Figure 2c. The experimental data were fitted with simple exponential functions, and we extracted propagation distances of 22 ± 5 µm and 42 ± 3 µm for SPP at 632 nm and 880 nm, respectively. Analytical calculations (see Supporting Information S0 for details) predict longer propagation distances: 42 µm at 632 nm and 155 µm at 880 nm for an ideal layer with the newly extracted permittivity. The propagation distance measurement at 632 nm proves that the JC data do not represent the lowest achievable loss in Ag. If the JC data were accurate at this wavelength, in fact, they would have predicted a propagation distance close to the measured one. We argue that this incidental agreement does not imply that our epitaxial Ag film is well modeled by JC data, because the scattering due to 1–2 monolayer roughness at the surface of the epitaxial film is expected to reduce the propagation distance from its theoretical limit derived from bulk optical constants. Although the propagation distance is not a direct verification of the measured permittivity values, our measurements confirm that the intrinsic loss of Ag is less than what is suggested by the JC data. Thus, the propagation distance measured is consistent with our newly extracted permittivity.

It is well known that the SPP propagation distance strongly depends on the film thickness. The excited SPP mode over a 45 nm thick film, which is confined at the Ag-oxide/air interface, partially resides inside the Ag film, but with substantial lower loss than JC’s values in the 1.8-2.5 eV range, while the control film shows values in between JC and Palik data. The residues in this region are small and centered around zero for all films, suggesting that our model fits the data very well. In the lowest energy range below 1.5 eV, the error becomes large due to reduced detector efficiency and our extracted ε₂ appears to be larger than that reported by JC. We note that the original JC data contain large errors in this same energy region (gray shadow in the Figure 1f–1h). Thus our measurements are consistent with JC’s in this lowest energy region.

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radiation loss into the substrate due to the thinness of the film. With a film thickness of 200 nm, for instance, the predicted propagation distance would increase to 247 µm at 632 nm and 755 µm at 880 nm, respectively. The SPP launching mechanism and expected modal profile is further verified by conducting full-wave simulations of the geometry (Figure 2d), employing the experimentally retrieved optical parameters (see Supporting Information S5 for details). In thermally evaporated films, the presence of grain boundaries limits the SPP propagation distance to a few micrometers in a thick film of 200 nm over the whole visible wavelength range. When a template stripping technique was applied, the SPP propagation distance was shown to improve significantly.\(^{[19]}\) The propagation distance extrapolated from our measurements far exceeds the theoretical limit (by a factor of ~10) quoted in the template stripping work, which included an unknown scattering length to account for the effect of grain boundaries.

The experimental realization of inherently lower loss (than previously expected) and the demonstration of greatly enhanced propagation length on epitaxial Ag films suggest promising prospects for epitaxial Ag as the improved plasmonic platform at visible frequencies. By using the retrieved intrinsic optical constants, we perform simulations to predict the performance of a metasurface and a plasmonic nano-laser.

**Figure 3a** shows a plasmonic metasurface composed of subwavelength dolmen-like nano apertures\(^{[20]}\) with dimensions outlined in the caption of Figure 3. This particular metasurface supports a high-Q spectral feature known as Fano resonance,\(^{[21,22]}\) a result of the interference between the bright dipole and the dark quadrupolar modes. The Fano resonance appears around 620 nm, clearly visible in the calculated reflection spectra (red curves, Figure 3a left y-axis). The use of epitaxial films only alters spectral properties near the Fano response, where fields are more concentrated in the metal and thus benefit more strongly from reduced losses. The Fano features are significantly sharper in the epitaxial case, as confirmed by calculating the derivative of the reflection intensity with respect to wavelength (black curves, Figure 3a right y-axis). We find significantly larger slopes near the Fano resonance of the metasurface with an increase of about three times in the derivative, a quantity of great interest for sensing applications.

**Figure 3b** shows the application of a single crystalline Ag shell to a plasmonic nano-laser.\(^{[23–25]}\) For simplicity we analyze a canonical plasmonic nano-laser, in the form of a core-shell spherical nanoparticle formed by a semiconductor gain medium with inverted Lorentzian dispersion 

\[
\epsilon_e = \epsilon_\infty + \frac{\omega_p^2}{\omega^2 + i\omega\gamma - \omega_0^2},
\]

where \(\omega_p = 2.0, \omega_0 = 2\pi 550\ THz, \gamma = 2\pi 80\ THz.\) The gain medium is covered by a thin Ag shell, with geometry \(a_s = 40\ nm, \sigma/a_s = 0.85.\) We plot the frequency dispersion of the normalized polarizability \(\alpha = \left[ \frac{6\omega e_\infty}{k_0} \right],\) where \(k_0\) is the free-space wavenumber and \(\epsilon_\infty\) is the corresponding permittivity. The polarizability essentially measures the scattering efficiency of the particle around its resonance frequency. We tuned the geometry to support a plasmonic resonance around the material resonance \(\omega_0\) of the gain material. The thinner lines in the figure show the case with no gain (\(\omega_0 = 0\)) for reference, and the thicker lines refer to the case when a moderate gain factor is considered (\(\omega_0 = 2\pi 100\ THz\)). It is seen that the single crystalline Ag in both cases is able to boost the resonance lineshape and increase the overall polarizability around the plasmonic resonance. Even more interestingly, when gain is considered in this geometry, the core is able to both compensate for the single crystalline Ag losses and to boost the level of normalized \(\text{Im} [\alpha]\) above the lasing threshold \(6\alpha e_\infty/k_0^2\) at resonance, which is a fundamental limit for passive nanostructures. In contrast, lasing cannot be achieved in the proposed core-shell structure when higher loss in Ag is incorporated. Our calculation suggests that single crystalline Ag may be ideal in realizing efficient subwavelength lasers based on plasmon resonances, due to the reduced level of losses and absorption, and therefore the reduced level of gain required to lase. The qualitative conclusion from our simple model calculation is consistent with the recently demonstrated\(^{[26]}\) superior performance of a plasmonic nano-laser based on epitaxial Ag films.

We highlight two caveats in interpreting the results of the above simulations. First, we evaluated the improved performance of these devices by simply replacing the optical constants...
reported by JC with the new optical constants extracted from our epitaxial films. In practice, most thermally evaporated films exhibit loss significantly higher than that reported by JC in the optical frequency range. Second, the new optical constants do not capture all advantages offered by single crystalline Ag films. In the case of SPP propagation distance, the elimination of grain boundaries increases propagation distance by two orders of magnitude compared to that found in thermal films. This increase in SPP propagation distance is partially responsible for the reduced mode volume and remarkably low lasing threshold of plasmonic nanolasers based on epitaxial Ag films.\(^\text{[6,26]}\) These two factors suggest that the overall advantages of using epitaxially grown Ag in plasmonic applications are more substantial than what is captured in the above calculations.

We suggest that future theoretical calculations on metamaterials and plasmonic devices based on Ag should incorporate the new optical constants reported here (see Table S1 in Supporting Information S5 for a list of numerical values), as they better capture the intrinsic properties of bulk Ag. Because we were able to fit the experimental data with a simple, three-component analytical model, these newly extracted optical constants will facilitate the calculation of other important parameters such as the material Q-factor and group velocity in Ag. While the reported optical constants would not apply to low-quality films produced using thermal evaporations, Ag nanoparticles,\(^\text{[27]}\) nanoshell,\(^\text{[28]}\) and nanoplatelets\(^\text{[29]}\) synthesized using wet chemical procedures are considered to be of single crystalline structure, for which these new optical constant values are expected to apply. We anticipate that these high-quality epitaxial silver films and their improved optical properties will have a significant positive impact on the fields of plasmonics and metamaterials as already demonstrated in the case of nanolasers.\(^\text{[6]}\)

**Supporting Information**

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

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