# ACS APPLIED NANO MATERIALS

# Tailoring the Optical Properties of Nanoscale-Thick Metal–Dielectric Ag–SiO<sub>2</sub> Nanocomposite Films for Precision Optical Coating Integration

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<20 nm in thickness can result in non-ideal process-dependent film uniformity and morphology that prevent controlled and repeatable ultrathin-film optical properties and behavior. Such thickness limitations undesirably constrain the design and integration of thin-metal films into high-precision multilayer optical coatings (e.g., narrow bandpass filters and induced transmission filters). The co-sputtering of nanocomposite



metal-dielectric films offers an appealing route toward ultrathin film coalescence and tailorable optical properties to achieve highprecision optical performance at significantly reduced film thicknesses (e.g., as compared to conventional all-dielectric multilayer optical media). In this work, silver (Ag) nanoparticles and contiguous Ag networks embedded in a silicon dioxide (SiO<sub>2</sub>) matrix were prepared at ambient substrate temperature via magnetron co-sputtering in a controlled pure argon atmosphere. We show that the structural features and optical properties of nanocomposite Ag-SiO<sub>2</sub> films can be manipulated by varying the co-sputtering duration at  $\sim$ 3–10 nm film thicknesses. Here, the Ag material phase ranges in structure from dispersed nanoparticles to contiguous partially coalesced networks. A distinct optical response transition occurs upon Ag phase transition from nanoparticles to the partially coalesced network. Large differences in the measured optical intensity are observed at these reduced film thicknesses: maximum  $\Delta T$ = 67%,  $\Delta R$  = 28%, and  $\Delta A$  = 46% in the visible and near-infrared regions. Overall, our work shows the tailoring of ultrathin-metalfilm optical properties (i.e., the refractive index, n, and extinction coefficient, k) and is expected to provide implementable methodologies toward the design, deposition, and integration of next-generation complex index multilayer optical filters and mirrors exhibiting enhanced precision spectral performance.

**KEYWORDS:** metal-dielectric, metallo-dielectric, nanocomposite, optical coatings, refractive index, thin-metal film, ultrathin film

## 1. INTRODUCTION

Metals embedded in ceramic or dielectric matrices have been demonstrated in thin-film optical applications ranging from optoelectronic devices, optical filters, super-resolution optical imaging, solar selective absorption coatings, miniaturized metallic waveguides, to optical sensing devices.<sup>1-10</sup> A mixed materials approach is likely the basis of electronic and optoelectronic transparent conductive oxides such as indium tin oxide, niobium zinc oxide, or aluminum zinc oxide.<sup>11-16</sup> Additionally, similar hybrid optical material tailoring is the appeal of complex mixed-valent oxides such as Nb<sub>x</sub>Mo<sub>y</sub>O<sub>z</sub> or  $Mo_x Ge_v O_z$ .<sup>3,17,18</sup> In the case of nano- and microstructured inhomogeneous material mixing, metal-dielectric hybrid films present the ability to engineer controlled structurally dependent light-matter interactions at reduced film thickness dimensions. For example, mixed metal-oxide  $M_x Si_y O_z$  (where M is a transition metal) thin films have been shown to yield tailored compositional-structural coloration for ophthalmic lenses.<sup>3</sup> Similarly, plasmonic nanoporous metals have been

prepared using heterogeneous co-deposition and selective dealloying techniques to improve surface plasmon-enhanced spectroscopy and photocatalytic applications (as compared to bulk non-porous metal films).<sup>7,19</sup> Overall, the process control of such heterogeneous coatings presents an appealing approach to generate composite ultrathin films (i.e., ≲10 nm in thickness) of metal nanoparticles and contiguous partially coalesced metal networks embedded within a dielectric material matrix. The optical property manipulation of such mixed metal-dielectric ultrathin films is the focus of this work and the potential integration (i.e., with respect to optical

Received: February 24, 2023 Accepted: April 17, 2023 Published: May 1, 2023





property range and ease of deposition) of such films into highprecision optical coating technologies. We demonstrate a broad range of light-matter manipulations resulting in localized nanoparticle peak absorptance spectral characteristics as well as bulk-like metallic optical properties (i.e., refractive index, *n*, and extinction coefficient, *k*) at ~3-10 nm film thicknesses—illustrating the potential utility of representative complex index metal-dielectric ultrathin films in precision multilayer optical coating media and optoelectronic devices (e.g., narrow bandpass filters, induced transmission filters, ophthalmic lenses, and photovoltaic devices).

The selected deposition technique to generate thin metal films can induce process-dependent film properties and has been observed in material-dependent physical vapor deposition methodologies.<sup>20</sup> As such, it is necessary to understand such processing relationships to selectively engineer ultrathin-film optical behavior. Magnetron sputtering is a widely preferred deposition technique due to the ease of material processing and scalable manufacturability. Here, strong electric and magnetic fields are generated inside the magnetron (the plasma formed and confined to the source target) to physically deposit a given source material of interest. Charge accumulation is common with sputtering techniques, which can result in differences in deposited film morphological, optical, and electrical properties.<sup>21</sup> The variability of thin-metal film uniformity and morphology is also impacted by the given interfacial substrate chemistry-leading to potential film wetting, adhesion, and/or film uniformity issues.<sup>22</sup> Elevated substrate temperatures during deposition can sometimes help mitigate undesired surface wetting (tension or critical surface energy) issues;<sup>23</sup> however, an increase in substrate temperature is not always conducive to manufacturing constraints at scale. As such, controlled ambient substrate temperature thin-film growth methodologies are preferred in many manufacturing scenarios. Due to these representative processing challenges, it is common to deposit  $\gtrsim 20$  nm of a metallic film to generate bulk-like complex index material properties.<sup>24</sup> This is problematic, for example, when thin-metal-film layering is of interest in high-precision multilayer optical coatings, optoelectronic devices, or to generate controlled ultrathin-film plasmonic optical phenomena where <20 nm metal film thicknesses are required.<sup>25-29</sup> However, such films often exhibit Volmer-Weber or island (adatom cluster) nucleation growth at <20 nm film thicknesses. It is important to note that alternative deposition techniques are known to moderately overcome film wetting and/or coalescence of thin-metal films; for example, seedling layers and high-power impulse magnetron sputtering (HiPIMS).<sup>6,30–32</sup> However, seedling layers can present a compositional materials processing challenge at scale and HiPIMS techniques are not yet amenable to most large-scale production manufacturing capabilities. Furthermore, HiPIMS methodologies are still subject to interfacial substrate/film wetting and coalescence challenges at <20 nm film thicknesses.

Compared to other noble metals, thin-film silver (Ag) exhibits low resistivity and Ohmic loss due to a lower extinction coefficient (k) in the visible spectral regime.<sup>24,30,32,33</sup> As such, Ag is often the preferred complex index metal in high-performance multilayer optical filters and mirrors.<sup>24,34–36</sup> Successful incorporation of complex index metal or mixed metal–dielectric ultrathin films presents the potential for greater tailoring of optical transmission, reflectance, and absorptance behavior in the engineered design of multilayer optical coatings and devices.<sup>26</sup> For example, dielectric–metal–

dielectric stacks have been used in thin-metal-film transparent conductors, low-emissivity windows, and colored solar panels.<sup>9,13,31</sup> Despite exhibiting appealing optical properties, Ag will rapidly oxidize upon exposure to ambient or oxygenrich atmosphere, which presents a major processing challenge during reactive ion sputtering.<sup>31,32</sup> The formation of a native Ag-oxide will subsequently affect the optical response due to uncontrolled ambient oxidative dampening of near-field surface plasmon resonance behavior known to dictate far-field optical performance.<sup>37,38</sup> As a result, we sputter both Ag and SiO<sub>2</sub> in a pure argon (Ar) environment to better facilitate dynamic adjustment of the Ag content and structure and mitigate unrestrained formation of a non-self-terminating native Agoxide.

Independent control of multiple sputtering sources has been used for the sole control of Ag material growth in either SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> dielectric material matrices in complementary studies to date.<sup>2,39</sup> However, prior work lacks broader insight surrounding the potential range of controlled optical tailoring due to the Ag structure and thickness dimension via ultrathin film co-deposition. In this work, nanoparticle and partially coalesced contiguous network Ag in SiO<sub>2</sub> ultrathin films were prepared at ambient substrate temperature via independent control of magnetron sputtering powers and durations on separate SiO<sub>2</sub> and Ag source targets. The resulting Ag-SiO<sub>2</sub> films exhibit resonant absorptance peaks that red-shift to longer wavelengths with increasing nanoscale film thickness and Ag structural dimensionality. These changes in spectral characteristics are due to known dimension-dependent resonant plasmonic behavior (i.e., near-field-localized or nonlocalized plasmon resonances).<sup>40</sup> We show that dimensiondependent structural changes in Ag at ultrathin film thicknesses likewise correspond to incremental increases in broad ranging far-field optical responses in the ultraviolet (UV) to infrared (IR) regimes. The optical properties of these films were also derived to quantify changes in anomalous optical dispersion involving the refractive index (n) and extinction coefficient (k)as a result of process-controlled Ag structuring embedded in SiO<sub>2</sub>. The reported Ag-SiO<sub>2</sub> ultrathin-film optical properties are qualified in relation to experimentally determined film structural morphology, chemical composition, and electrical properties. Overall, our representative co-sputtering methodology illustrates a process-controlled composite metaldielectric approach toward complex index optical ultrathin films not easily achieved via conventional homogeneous thinmetal-film deposition practices.

#### 2. EXPERIMENTAL SECTION

2.1. Ag-SiO<sub>2</sub> Ultrathin-Film Deposition. Ag-SiO<sub>2</sub> ultrathin films were prepared using a custom stainless-steel high-vacuum chamber equipped with direct current (DC) magnetron sputtering (DCMS) and pulsed DC magnetron sputtering (PDCMS) capabilities. In this chamber configuration, two magnetron sputtering guns were tilted to a 20° angle (with respect to substrate normal) toward the center of the substrate surface. During film deposition, the chamber was initially pumped down to 50 mTorr by a mechanical roughing pump and further evacuated to a pressure of  $< 2 \times 10^{-7}$  Torr using a Varian turbomolecular pump connected to the chamber via an automated gate valve assembly. Without breaking deposition chamber vacuum, the samples were transferred into the deposition chamber through a load lock system. Prior to deposition, 1 in. diameter fused silica substrates (Machine Glass Specialists, Inc.) and 2 in. diameter silicon (100) prime graded substrates (p-type, University Wafer, Inc.) were cleaned with acetone, methanol, isopropyl alcohol, dried under



**Figure 1.** (a) Schematic representation of three-layer  $SiO_2/Ag-SiO_2/SiO_2$  deposited on a substrate where  $Ag-SiO_2$  deposition is shown as a function of increasing co-sputtering time, or  $t_{Ag-SiO_2}$  and (b) pictures of the  $Ag-SiO_2$  films on 1 in. diameter fused silica substrates for illustration. Note that  $t_{Ag-SiO_2} = 0$  s (or  $t_{SiO_2} = 20$  min) means there was no  $Ag-SiO_2$  co-sputtering included during the deposition and that the  $SiO_2$  sputtering parameters match those used for subsequent  $Ag-SiO_2$  co-sputtered films.

nitrogen gas, and then transferred to the sputtering chamber as described. Films prepared on optically transparent fused silica and optically non-transparent silicon substrates were processed at the same time.

The SiO<sub>2</sub> target (Kurt J. Lesker, 99.99% purity, 2 in. diameter  $\times$ 0.250 in. thickness) was placed in a Lesker Torus magnetron gun powered at 75 W with a pulse frequency of 150 kHz and a reversed pulse time of 1.0  $\mu$ s (85% duty cycle) using an Advanced Energy Pinnacle Plus pulsed DC power supply. The Ag target (Plasmaterials, Inc., 99.99% purity, 2 in. diameter × 0.250 in. thickness) was placed in an MeiVac MAK magnetron gun powered by an Advanced Energy MDX 500 DC power supply. Ultrahigh-purity argon (Ar, 99.999%) was introduced to the chamber through a port near the source targets and held at a 25 sccm constant mass flow rate (controlled by an MKS flow controller). The substrate was rotated at 12 rpm during film growth to improve lateral film uniformity over the substrate surface areas. All thin films were deposited at ambient substrate temperature during growth processes. A schematic representation of representative nanocomposite metal-dielectric Ag-SiO2 ultrathin films prepared in this work is shown in Figure 1a representing a stepwise coating procedure (i.e., SiO2-only thin films deposited above and below the Ag–SiO<sub>2</sub> layer). Note that the first deposited SiO<sub>2</sub> layer in Figure 1a is considered elementally similar to the fused silica substrates and native SiO<sub>2</sub> of the silicon substrates. The encapsulating sputtered SiO<sub>2</sub> layers serve to simplify the control of Ag-SiO<sub>2</sub> co-sputtering as well as prevent immediate Ag interfacial oxidation upon exposure to ambient atmosphere. Ag-SiO2 films at selected co-sputtering times  $(t_{Ag-SiO_2})$  deposited on 1 in. diameter fused silica substrates and pictures of film coloration differences (relative to sputtering time) are shown in Figure 1b.

The Ag–SiO<sub>2</sub> films were deposited in a stepwise fashion to reduce variability during the growth process. SiO<sub>2</sub> was first deposited ( $t_{SiO_2} = 10 \text{ min}$ ), followed by Ag–SiO<sub>2</sub> co-sputtering ( $t_{Ag-SiO_2} =$  selected durations discussed in the following), and then a SiO<sub>2</sub> top film ( $t_{SiO_2} = 10 \text{ min}$ ). The SiO<sub>2</sub> ultrathin films at these sputtering conditions are expected to be about ~1.5 nm in thickness. PDCMS was used in pure Ar plasma for the SiO<sub>2</sub> encapsulating layers. The frequency of the pulse was set at 150 kHz with a reverse time of 1  $\mu$ s. Without stopping the power to the SiO<sub>2</sub> target during the initial first film growth, the Ag–SiO<sub>2</sub> layer was prepared by magnetron co-sputtering times of  $t_{Ag-SiO_2} = 0$ , 15, 20, 30, 40, 60, and 90 s (see Figure 1b). Detailed deposition parameters used for fabricating the Ag–SiO<sub>2</sub> films are listed in Table S1. The first film serves as a reference where  $t_{Ag-SiO_2} = 0$  s, meaning no Ag–SiO<sub>2</sub> co-sputtering was performed during the

deposition and that the SiO<sub>2</sub> sputtering parameters match those used for subsequent Ag–SiO<sub>2</sub> co-sputtering (where  $t_{Ag-SiO_2} > 0$  s). As a result, this reference coating represents a SiO<sub>2</sub>-only film (or  $t_{SiO_2} = 20$ min) and is shown in Figure 1b for visual comparison. Note that the magnetron co-sputtering methodology discussed here is described in a complementary work.<sup>11,17,18</sup>

**2.2.** Scanning Electron Microscopy and X-ray Diffraction. Surface morphologies of the Ag-only and Ag-SiO<sub>2</sub> films were imaged using a FEI-Sirion scanning electron microscope in an ultrahigh resolution mode. The crystal structure of the Ag-SiO<sub>2</sub> films was investigated using grazing incidence X-ray diffraction (GIXRD) in  $2\theta$ scan mode (out-of-plane) using a Rigaku SmartLab X-ray diffractometer with a Cu K $\alpha$  ( $\lambda$  = 1.541862 Å) X-ray source (40 kV/44 mA). The grazing incident angle was set to  $\Omega$  = 0.35°. The GIXRD measurements were scanned in a  $2\theta$  range of 10-80° at a scan speed of 2° per minute with a step size of 0.01°. Quantitative analysis of the lattice spacing, peak positions, width, and crystallite size was done from the XRD patterns using Rigaku PDXL (v. 2.0) data processing software. Each film's thickness, surface roughness, and density were measured and obtained using the same Rigaku SmartLab from X-ray reflectivity (XRR) measurements.

**2.3.** X-ray Photoelectron Spectroscopy. Surface chemical composition of the Ag–SiO<sub>2</sub> films was determined from X-ray photoelectron spectroscopy (XPS) survey scans using a monochromatic Al K $\alpha$  source (1486.69 eV) at an analyzer pass energy of 160 eV (Kratos Axis Ultra DLD instrument). XPS high-energy resolution scans for C 1s, O 1s, Ag 3d, and Si 2s were carried out to obtain valence states of the Ag–SiO<sub>2</sub> films (with an analyzer pass energy of 40 eV). All high-energy resolution spectra were calibrated and referenced with respect to adventitious carbon, C 1s, at a binding energy (BE) of 284.8 eV.<sup>11,41</sup> The spectra were fit with Gaussian–Lorentzian line shapes after Shirley background subtraction. XPS spectra were analyzed using CasaXPS v.2.3.15 software.

**2.4.** UV-Vis-NIR Spectrophotometry. Optical transmission and reflection intensity measurements were carried out using a Cary 5000 UV-vis-near-IR (NIR) spectrophotometer (Agilent Technologies) in a wavelength range 200–2000 nm. Reflection spectroscopy was performed with a diffuse reflectance accessory consisting of a 150 mm integrating sphere and represents the total measured reflectance (i.e., specular and diffuse). Percent absorptance (A) was determined from the measured percent transmission (T) and percent reflectance (R) measurements by 100% = T + R + A or A = 100% - T - R.

**2.5. Variable-Angle Spectroscopic Ellipsometry.** The film thicknesses and optical properties of the Ag–SiO<sub>2</sub> films on fused silica substrates were evaluated simultaneously with an ex situ variable angle spectroscopic ellipsometer (Alpha-SE by J.A. Woollam) operating in a



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Figure 2. SEM micrographs of the (a-c) Ag-only and (d-i) Ag-SiO<sub>2</sub> films deposited on silicon substrates for representative  $t_{Ag}$  and  $t_{Ag-SiO_2}$ .

wavelength range of 371–900 nm. Spectroscopic ellipsometry data were appended with transmission intensity spectral data from the UV–vis–NIR measurements in a wavelength range of 200–2000 nm. The spectroscopic ellipsometry data, involving the magnitude ( $\Psi$ ) and phase difference ( $\Delta$ ) of the reflected incident polarized light, were measured at two incident angles of 70 and 75°. The film thickness (d), refractive index (n), and extinction coefficient (k) for each film were derived by fitting both  $\Psi$  and  $\Delta$  optical dispersion and transmission intensity data sets. Optical data analysis involved a model containing a Cauchy ( $t_{Ag-SiO_2} = 0$  s), a Tauc–Lorentz or one (or more) Lorentz oscillator(s) ( $t_{Ag-SiO_2} = 15-40$  s), or an additional Drude oscillator ( $t_{Ag-SiO_2} = 60$  and 90 s). The complex refractive indices ( $\tilde{n} = n + ik$ , where  $\varepsilon_1 = n^2 - k^2$  and  $\varepsilon_2 = 2nk$  for the real and imaginary parts of the complex dielectric function,  $\tilde{\varepsilon}$ , respectively) of the Ag–SiO<sub>2</sub> films were derived from the formalisms given by

$$n(E) = A + \frac{B}{E} + \frac{C}{E} + \dots$$
 (1)

$$\tilde{\varepsilon}(E) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_0 - \sum_{k=1}^N \frac{f_k}{E_k^2 - E^2 - iE\gamma_k}$$
(2)

$$\varepsilon_{2}(E) = \begin{cases} \frac{f_{k}\gamma_{k}E_{k}(E - E_{gk})^{2}}{(E^{2} - E_{k}^{2})^{2} + \gamma_{n}^{2}E^{2}} \cdot \frac{1}{E}, & \text{if } E > E_{gk} \\ 0, & \text{if } E \le E_{gk} \end{cases}$$
(3)

and

$$\tilde{e}(E) = e_1 + ie_2 = e_0 - \sum_{k=1}^{N} \frac{f_k}{E_k^2 - E^2 - iE\gamma_k} - \frac{\omega_p^2}{E^2 + iE\tau_p}$$
(4)

The Cauchy model is defined by eq 1, the Lorentz model by eq 2, the comparative Tauc-Lorentz model by eq 3, and the Drude-Lorentz model by eq 4.<sup>42</sup> In eq 1, n is the refractive index, E is the energy, and A, B, C, etc., are coefficients that can be determined via fitting the equation to the measured  $\Psi$  and  $\Delta$  optical dispersion data. Note that k(E) is assumed to be 0 when using the conventional Cauchy model, as is the case here for  $t_{Ag-SiO_2} = 0$  s ( $t_{SiO_2} = 20$  min). In eqs 2-4,  $\varepsilon_0$  is the permittivity of free space,  $f_k$  is the resonant oscillator amplitude strength,  $\gamma_k$  is the resonant peak oscillator width, and  $E_k$  is the resonant peak oscillator energy for the kth oscillator.<sup>43</sup> Equation 3 illustrates the assumptions (compared to the conventional Lorentz oscillator given by eq 2) for the Tauc-Lorentz formalism involving  $\varepsilon_{2}$ , where  $E_{g}$  is the band gap. For the Drude component in eq 4,  $\omega_{\rm p}$  is the plasma frequency and  $\tau_{\rm p}$  is the scattering time (or the effective Drude decay constant). Each equation is written as a function of energy (E) for simplicity, but our results are represented as wavelengths ( $\omega$  or  $\lambda$ ) throughout. Detailed spectroscopic ellipsometry fit parameters for all films are provided in Table S3. Spectroscopic ellipsometry data analysis was carried out using CompleteEASE v.4.07 software.

## 3. RESULTS AND DISCUSSION

**3.1.** Ag–SiO<sub>2</sub> Film Morphology.  $Ag-SiO_2$  co-deposition as a function of time  $(t_{Ag-SiO_2})$  greatly influences the morphology of metal–dielectric ultrathin films (compare Figure 1a) and associated optical properties (discussed in Section 3.4). Morphological characterization is therefore paramount to identify the structural feature influence on the reported optical properties and, in this case, processing control range involving DCMS and PDCMS co-sputtering conditions. For comparison, the ultrathin-film composite morphologies of sputtered Ag-only and co-sputtered Ag–SiO<sub>2</sub> are provided in Figure 2. Ag-only film morphology is shown for comparison and were deposited on silicon substrates (having a native SiO<sub>2</sub> interfacial layer) by DCMS with Ag-only deposition times  $(t_{Ag})$ of 15, 60, and 120 s (see Figure 2a-c for scanning electron microscopy, SEM, images). DCMS of the Ag-only films serve as an example to illustrate the processing challenges that can occur involving the sputtering of thin-metal films as discussed. These Ag-only films likewise help emphasize the need to develop processing methodologies at ambient substrate temperature with improved thin-film uniformity and coalescence. Note that  $t_{Ag}$  are representative of sputtering conditions employed during the co-deposition of Ag-SiO<sub>2</sub> films (i.e., ambient substrate temperature, substrate interfacial chemistry, and sputtering parameters). Figure 2d-i shows SEM micrographs of the co-sputtered Ag-SiO<sub>2</sub> films deposited on silicon substrates at selected co-sputtering times  $(t_{Ag-SiO_2})$ . Here, Figure 2d-i shows that the Ag-SiO<sub>2</sub> films appear more uniform, dense, and smooth compared to the Ag-only films in Figure 2a-c. Figure 2d-i also shows Ag nanoparticles uniformly dispersed in the SiO<sub>2</sub> matrix at  $t_{Ag-SiO_2} = 15-40$  s, which transition to Ag partial coalescence at  $t_{Ag-SiO_2} = 60$  and 90 s. Overall, the partial coalescence of Ag–SiO<sub>2</sub> films occur at early sputtering times, leading to fairly uniform and controlled morphology at ultrathin film thicknesses (discussed more in the next section).

3.2. Ag–SiO<sub>2</sub> Film Crystalline Structure. Ag–SiO<sub>2</sub> film morphology will be influenced by the resulting crystalline structure of the mixed materials, which is induced and influenced by the co-sputtering conditions employed. GIXRD patterns of the Ag-SiO<sub>2</sub> nanocomposite films deposited on fused silica substrates are shown in Figure S1. These data suggest the Ag-SiO<sub>2</sub> films are in an amorphous phase for  $t_{Ag-SiO_2} = 15$  s where the Ag nanoparticle content is low, well isolated, and well dispersed in the SiO<sub>2</sub> matrix. For  $t_{Ag-SiO_2} \ge$ 20 s, a preferred orientation of Ag(111) appeared and increased in intensity with  $t_{Ag-SiO_2}$  as the crystallite sizes increased. The intensity reached a maximum for  $t_{\rm Ag-SiO_2} = 60$  s where Ag onset partial coalescence occurs. The Ag(111) orientation shifted from  $2\theta$  = 37.91° at  $t_{Ag-SiO_2}$  = 20 s to  $2\theta$  =  $38.39^{\circ}$  for  $t_{Ag-SiO_2} = 60$  s. The weaker peaks for the Ag(200), (220), and (103) orientations appeared at  $2\theta = 44.14$ , 64.70, and 77.48°, respectively, for  $t_{Ag-SiO_2} = 60$  and 90 s. This indicates that these Ag-SiO2 ultrathin films are polycrystalline upon Ag partial coalescence (as compared to the films with isolated and dispersed Ag nanoparticles).

The increase of the (111) peak intensity and the subsequent decrease of the full width at half maximum (FWHM),  $\beta$ , for  $t_{Ag-SiO_2}$  from 20 to 90 s suggests that the crystallinity of the Ag–SiO<sub>2</sub> films improved with increased Ag–SiO<sub>2</sub> content (see Table 1). The overall minimum  $\beta$  is 1.38° for  $t_{Ag-SiO_2} = 90$  s and corresponds to larger crystallite sizes due to Ag coalescence (i.e., the contiguous network of Ag tendril-like features). The nanocrystallite sizes, D(111), at the (111) orientation are calculated from the Scherrer equation where Ag nanocrystallite size (1.3–6.4 nm) increases with increasing  $t_{Ag-SiO_2}$  (i.e., 20–90 s, see Table 1). The Ag–SiO<sub>2</sub> film deposited at  $t_{Ag-SiO_2} = 90$  s displayed the largest crystallite size and the narrowest  $\beta$ , representing ideal crystallinity for this series of co-sputtered Ag–SiO<sub>2</sub> ultrathin films.

Table 1. Lattice Constants  $(l_c)$ ,  $2\theta(111)$ ,  $\beta(111)$ , and D(111) Ag Crystallite Sizes from the (111) Orientation Determined from the GIXRD Measurements

$t_{Ag-SiO_2}$ (s)	$l_{\rm c}$ (Å)	$2\theta(111)$	$\beta(111)$	D(111) (nm)
20	$2.25 \pm 0.01$	37.91 ± 0.02	$1.9 \pm 0.2$	$1.3 \pm 0.2$
30	$2.36\pm0.01$	$38.11 \pm 0.08$	$1.8 \pm 0.1$	4.8 ± 0.3
40	$2.36\pm0.01$	$38.10 \pm 0.06$	$1.6 \pm 0.1$	$5.4 \pm 0.2$
60	$2.34\pm0.01$	$38.39 \pm 0.03$	$1.5 \pm 0.1$	$5.7 \pm 0.1$
90	$2.35\pm0.01$	$38.27 \pm 0.03$	$1.4 \pm 0.1$	$6.4 \pm 0.1$

Table 2. Film Thickness (d), Surface Roughness (Sr), and Film Density ( $\sigma$ ) Obtained from 1-Layer Model XRR Analysis

$t_{Ag-SiO_2}$ (s)	<i>d</i> (nm)	Sr (nm)	$\sigma$ (g/cm <sup>3</sup> )
0	$3.06 \pm 0.03$	$0.78 \pm 0.01$	$2.41 \pm 0.01$
15	$3.95 \pm 0.01$	$0.99 \pm 0.01$	$4.55 \pm 0.02$
20	$4.19 \pm 0.01$	$0.86 \pm 0.01$	$4.46 \pm 0.02$
30	$6.34 \pm 0.01$	$1.01 \pm 0.01$	$5.26 \pm 0.02$
40	$7.46 \pm 0.03$	$0.79 \pm 0.01$	$6.00 \pm 0.01$
60	$8.42 \pm 0.02$	$0.73 \pm 0.01$	$7.24 \pm 0.01$
90	$10.04 \pm 0.01$	$1.23 \pm 0.01$	$8.73 \pm 0.02$

As shown in Table 2, the film thickness (d), surface roughness (Sr), and film density ( $\sigma$ ) derived from XRR analysis changed with increasing  $t_{Ag-SiO_2}$  for 20–90 s. The total film thickness increased from 3.06 to 10.04 nm and the film density from 2.41 to 8.73 g/cm<sup>3</sup> with increasing  $t_{Ag-SiO_2}$  of 20– 90 s (see Figure S2). The XRR patterns were fit with approximated 1-layer and 2-layer models as shown in Figure S3 for  $t_{Ag-SiO_2}$  = 30, 40, and 90 s. The film thicknesses ( $d_1$  and  $d_2$ ), surface roughnesses (Sr<sub>1</sub> and Sr<sub>2</sub>), and film densities ( $\sigma_1$  and  $\sigma_2$ ) derived from the approximated 2-layer XRR model analysis are listed in Table S2. The 2-layer XRR model was used in selected cases as it results in better fitting due to the bottom layer filled with high Ag density and the top layer with a lower density. Note that the deposition rate for SiO<sub>2</sub> is relatively slow at 0.25 nm/min in this work; however, we observed that the plasma from PDCMS of the  $\mathrm{SiO}_2$  target in pure Ar helps to prevent the sputtered Ag atoms from agglomerating upon deposition at the substrate surface. In the pure Ar atmosphere, the SiO<sub>2</sub> atoms in the plasma help facilitate Ag smoothening and coalescence at thinner Ag thickness at the substrate interface.<sup>6</sup> As a result, co-sputtering of Ag and SiO<sub>2</sub> promotes the formation of more uniform Ag nanoparticles dispersed in the  $SiO_2$  matrix (<8 nm thickness) and subsequent Ag contiguous network coalescence (8-10 nm thickness) at ultrathin film thicknesses.

**3.3.** Ag–SiO<sub>2</sub> Film Chemical Composition. Another potential contribution to the observed Ag–SiO<sub>2</sub> film structural morphology and crystallinity is the elemental composition (e.g., controlled heterogeneity and mitigation of mixed interlayer regions or Ag oxidation). In this work, XPS was used to investigate the chemical composition of the Ag–SiO<sub>2</sub> films prepared at selected  $t_{Ag-SiO_2}$ . The survey scans and high-energy resolution XPS spectra of the carbon (C 1s), oxygen (O 1s), silver (Ag 3d), and silicon (Si 2s) were carried out for the films deposited on silicon substrates (compare Figures S4–S6). Oxygen (O 1s), silver (Ag 3d), and silicon (Si 2s) atomic

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#### Table 3. Chemical Composition of the SiO<sub>2</sub>-Only, Ag-Only, and Ag-SiO<sub>2</sub> Films from High-Energy Resolution XPS Analysis

<i>t</i> (s)	transition	composition (at. %)	BE (eV)	FWHM (eV)	O/Si	Ag/Si
$t_{Ag-SiO_2} = 0$	C 1s	9.7	284.8 ± 0.1		2.01	0
	O 1s	60.3	$532.4 \pm 0.1$	$1.52 \pm 0.01$		
	Ag 3d					
	Si 2s	28.2	$155.0 \pm 0.1$	$2.37 \pm 0.04$		
$t_{Ag} = 15$	C 1s	32.5	$284.8 \pm 0.1$		1.19	0.57
	O 1s	29.0	$532.2 \pm 0.1$	$1.53 \pm 0.04$		
	Ag 3d	13.9	$368.6 \pm 0.1$	$0.98 \pm 0.03$		
	Si 2s	24.6	$153.7 \pm 0.1$	$2.41 \pm 0.05$		
$t_{\rm Ag-SiO_2} = 15$	C 1s	22.7	$284.8 \pm 0.1$		2.23	0.25
	O 1s	51.1	$532.5 \pm 0.1$	$1.55 \pm 0.05$		
	Ag 3d	5.6	$368.3 \pm 0.1$	$1.02 \pm 0.02$		
	Si 2s	22.2	$154.2 \pm 0.1$	$2.48 \pm 0.06$		
$t_{\rm Ag-SiO_2} = 20$	C 1s	23.5	$284.8 \pm 0.1$		2.35	0.48
	O 1s	50.8	$532.3 \pm 0.1$	$1.54 \pm 0.02$		
	Ag 3d	8.2	$368.3 \pm 0.1$	$0.99 \pm 0.01$		
	Si 2s	20.4	$154.2 \pm 0.1$	$2.32 \pm 0.03$		
$t_{Ag-SiO_2} = 30$	C 1s	27.0	$284.8 \pm 0.1$		2.98	0.99
	O 1s	45.4	$532.7 \pm 0.1$	$1.57 \pm 0.02$		
	Ag 3d	14.9	$368.7 \pm 0.1$	$1.26 \pm 0.06$		
	Si 2s	13.1	$154.4 \pm 0.1$	$2.22 \pm 0.04$		
$t_{\rm Ag-SiO_2} = 40$	C 1s	18.3	$284.8 \pm 0.1$		2.46	0.38
	O 1s	55.3	$532.6 \pm 0.1$	$1.57 \pm 0.02$		
	Ag 3d	8.1	$368.3 \pm 0.1$	$0.91 \pm 0.02$		
	Si 2s	21.3	$154.2 \pm 0.1$	$2.39 \pm 0.01$		
$t_{Ag-SiO_2} = 45$	C 1s	18.6	$284.8 \pm 0.1$		2.68	0.52
	O 1s	51.9	$532.6 \pm 0.1$	$1.58 \pm 0.01$		
	Ag 3d	10.1	368.6 ± 0.1	$1.16 \pm 0.06$		
	Si 2s	19.4	$154.2 \pm 0.1$	$2.37 \pm 0.02$		
$t_{\rm Ag-SiO_2} = 60$	C 1s	14.8	$284.8 \pm 0.1$		2.73	0.41
	O 1s	56.2	$532.6 \pm 0.1$	$1.56 \pm 0.01$		
	Ag 3d	8.4	$368.4 \pm 0.1$	$0.96 \pm 0.01$		
	Si 2s	20.6	$154.2 \pm 0.1$	$2.33 \pm 0.03$		
$t_{Ag-SiO_2} = 90$	C 1s	16.7	$284.8 \pm 0.1$		3.12	1.68
	O 1s	44.8	$532.4 \pm 0.1$	$1.58 \pm 0.02$		
	Ag 3d	24.1	$368.3 \pm 0.1$	$0.76 \pm 0.01$		
	Si 2s	14.4	$154.1 \pm 0.1$	$2.39 \pm 0.07$		

concentrations were measured and averaged over three positions for each sample to determine the chemical composition of the Ag–SiO<sub>2</sub> films (see Table 3). XPS survey spectra for  $t_{Ag-SiO_2} = 0$ , 40, and 90 s are shown in Figure S7 in a binding energy range of 0–1200 eV. All high-energy resolution spectra were calibrated and referenced to the adventitious carbon (C 1s) peak at 284.8 eV.

The binding energies of Ag  $3d_{5/2}$  in the films were  $368.4 \pm 0.1 \text{ eV}$  with a narrow FWHM peak-height of  $1.0 \pm 0.2 \text{ eV}$ , confirming neutral Ag<sup>0</sup> for all Ag–SiO<sub>2</sub> films in this work. Two Si 2s peaks appeared on the SiO<sub>2</sub> film  $(t_{\text{Ag-SiO}_2} = 0 \text{ s})$  at 154.0  $\pm 0.1$  and 149.7  $\pm 0.1$  eV corresponding to the oxidation states of Si from the native SiO<sub>2</sub> film and, at a low binding energy, from the silicon substrate (due to a very thin native 1–2 nm SiO<sub>2</sub> film). With increasing  $t_{\text{Ag-SiO}_2}$ , the Si<sup>0</sup> peak greatly decreased and disappeared in the measurements (i.e., at  $t_{\text{Ag-SiO}_2} = 90 \text{ s}$ ) as the Ag coalesced within the SiO<sub>2</sub> matrix and more completely covered the Si substrate surface. The binding energies of O 1s appeared at 532.6  $\pm 0.1$  eV and represent oxygen binding to Si in fully stoichiometric SiO<sub>2</sub>. Overall, XPS

analysis suggests no Ag oxidation occurs during the ultrathin film co-sputtering growth process.

For the Ag-only film ( $t_{Ag} = 15$  s), the XPS spectrum shows the presence of Si plasmon peaks, indicating that the Ag-only film is not homogeneous on the Si substrate with parts of the substrate surface exposed. This is in agreement with the SEM micrographs in Figure 2, which also show that the Ag-only film is uncoalesced, aggregated, and nonuniform. The relative intensities of the Si 2p components from SiO<sub>2</sub> and Si in the high-energy resolution Si 2p spectra indicate that this native SiO<sub>2</sub> layer is approximately 0.45 nm thick for the elemental Si substrate. With respect to the deposited SiO<sub>2</sub>, the total thickness of the SiO<sub>2</sub> layer is calculated to be ~1.55 nm. Note that the O 1s intensity reduces as the Ag-SiO<sub>2</sub> deposition time increases (only  $t_{Ag-SiO_2} = 40$  and 90 s are shown for comparison in Figure S7).

The modified Auger parameter from the survey scans of the  $Ag-SiO_2$  film deposited for 90 s is 726.4 eV and in good agreement with the NIST database and the Handbook of X-ray Photoelectron Spectroscopy for metallic silver.<sup>41,44</sup> It is important to note there is a decrease in the modified Auger

parameter of about 1.5-2.0 eV when going from Ag-metal to Ag-oxide, but no such decrease in the modified Auger parameter for the 90 s deposition of Ag-SiO<sub>2</sub> was observed. Overall, our XPS analysis shows that no significant Ag oxidation occurs during our co-sputtering growth process, and ultrathin film growth can be well-controlled under such processing conditions.

3.4. Ag-SiO<sub>2</sub> Film Optical Properties. Film property characterization involving the morphology, crystallinity, and elemental composition illustrates the high-precision control of our co-sputtering approach employed for ultrathin-film nanocomposite Ag-SiO2. Here, we illustrate the corresponding optical responses and properties of these highly processcontrolled ultrathin films. Figure 3 shows the optical percent transmission (T), reflectance (R), and absorptance (A) spectra (where A = 100% - T - R) as a function of wavelength (200-2000 nm) for the Ag–SiO<sub>2</sub> films deposited at selected  $t_{Ag-SiO_2}$ . An absorptance peak appears in the UV regime for each nanoparticle composite film and shifts from 430, 448, 485, to 510 nm with increasing  $t_{Ag-SiO_2}$  (i.e., for 15, 20, 30, to 40 s, respectively). Additionally, a corresponding increase in peak absorptance width occurs with increasing  $t_{Ag-SiO_2}$  (due to the corresponding Ag nanocrystallite size increase with respect to the interband transition for Ag at ~310 nm).<sup>45</sup> At  $t_{Ag-SiO_2} = 60$ and 90 s, the Ag in the Ag-SiO<sub>2</sub> films partially coalesce and became a contiguous network vs isolated nanoparticles (with tendril-like width dimensions much smaller than the incident wavelength of light). For these films, the optical transmission no longer increases in the NIR and shortwave IR regions as the films begin to resemble more bulk-like thin-film silver properties. Also, note that the color of the films on the fused silica substrates (Figure 1b) changes from clear to light yellow, yellow, peach, light purple, purple, blue, and blue gray as  $t_{Ag-SiO_2}$  increases, which corresponds to the optical responses observed in Figure 3 and chromaticity coordinates in Figure 4. Such changes in far-field optical intensity spectral behavior correspond to known near-field changes of localized and nonlocalized surface plasmon resonances (i.e., Ag nanoparticle size and transition to a contiguous Ag network).<sup>40,46</sup> The chromaticity coordinates in Figure 4 are evaluated in transmission involving the three-layer SiO<sub>2</sub>/Ag-SiO<sub>2</sub>/SiO<sub>2</sub> deposited on fused silica and agree with responses in Figure 3a. The chromaticity diagram was prepared using LayersPro (Table Mountain Optics), a custom optical coating design software.

To further quantify the observed changes in optical behavior due to differences at selected  $t_{Ag-SiO_2}$ , the optical properties of these metal-dielectric Ag-SiO<sub>2</sub> nanocomposite films were derived using variable angle spectroscopic ellipsometry. Here, the three SiO<sub>2</sub>/Ag-SiO<sub>2</sub>/SiO<sub>2</sub> layers (see Figure 1a) deposited on fused silica substrates were used in the optical dispersion models. However, the optical dispersion data analysis was simplified to assume Ag-SiO<sub>2</sub> resides on top of the first deposited SiO<sub>2</sub> layer (~1.5 nm, on the fused silica substrate surface) and Ag-SiO<sub>2</sub> is capped with the same deposited SiO<sub>2</sub> layer (~1.5 nm). This agrees with the ultrathin SiO<sub>2</sub> film at  $t_{Ag-SiO_2} = 0$  s (or  $t_{SiO_2} = 20$  min) being ~3 nm and represents the total combined thickness of the top and bottom SiO<sub>2</sub>-only layers (i.e., without the middle Ag-SiO<sub>2</sub> layer, see XRR results in the Supporting Information and Table 2).



**Figure 3.** (a) Transmission, (b) reflectance, and (c) absorptance spectra of the Ag-SiO<sub>2</sub> films deposited at selected  $t_{Ag-SiO_2}$ . Absorptance was calculated from A = 100% - T - R (see the Experimental Section).

The ~3 nm thick SiO<sub>2</sub> film ( $t_{Ag-SiO_2} = 0$  s or  $t_{SiO_2} = 20$  min) was fit with a simple one-layer Cauchy model (eq 1) on a fused silica substrate. Due to the ultrathin thickness of the SiO<sub>2</sub> film, it is paramount to determine the approximate film thickness outside of ellipsometry data derivation to improve the



**Figure 4.** Chromaticity coordinates (CIE 1931) of the Ag–SiO<sub>2</sub> films from  $t_{Ag-SiO_2} = 15$  to 90 s evaluated in transmission. Compare Figure 3a for experimental transmission spectra.

uniqueness of the fit. Here, we used the XRR film thickness results to fix the approximate film thicknesses during ellipsometry optical dispersion data analysis to ensure a robust solution of the resulting optical constants (i.e., refractive index, *n*, and extinction coefficient, *k*). The thicknesses of all  $SiO_2$ layers were fixed at 1.5 nm, and these layer optical constants were the same as that of the SiO<sub>2</sub>-only film ( $t_{Ag-SiO_2} = 0$  s). The middle layer of the nanoparticle Ag-SiO<sub>2</sub> films prepared at  $t_{Ag-SiO_2} = 15-40$  s was analyzed with a Tauc-Lorentz oscillator and a Lorentz oscillator described in eqs 2 and 3, respectively. An additional Drude oscillator (eq 4) was added for the partially coalesced Ag–SiO<sub>2</sub> films prepared at  $t_{Ag-SiO_2}$  = 60-90 s. The absence of a Drude oscillator in the other films further suggests no Ag coalescence, while the addition of the Drude oscillator in the model for these films suggests coalescence (where film resistivity can be derived). In this work, all spectroscopic ellipsometry data were appended with the experimental percent transmission data (weighted at 300%) from UV-vis-NIR spectrophotometry in the wavelength range of 200-2000 nm (the fit parameters are provided in Table S3). This appended modeling approach results in a much better approximation of the complex index (i.e., both nand k for anomalous dispersion) Ag-SiO<sub>2</sub> films. Figure 5 shows the derived wavelength-dependent refractive index and extinction coefficient for each Ag-SiO2 layer at the selected  $t_{Ag-SiO_2}$ . The derived refractive indices in Figure 5a show complementary spectral characteristics observed in Figure 3. Likewise, the derived extinction coefficients in Figure 5b illustrate similar spectral absorptance characteristics as observed in Figure 3c. Figure 5b also shows a subtle increase in *k* toward NIR and shortwave IR regions for  $t_{Ag-SiO_2} = 60-90$ which suggests presumed percolation from partial s, coalescence (and/or long-range resonant plasmon coupling) in these films despite the observation of incomplete, or full, coalescence (see Figure 2h-i).<sup>29,47</sup> The resistivity of the partially coalesced Ag-SiO<sub>2</sub> films is derived from the ellipsometry fits, which utilize a Drude-Lorentz formalism. The Drude component of the model yields responses on the order of  $1.89 \times 10^{-3} \Omega$  cm for  $t_{Ag-SiO_2} = 60$  s and decreased to



**Figure 5.** (a) Refractive index, *n*, and (b) extinction coefficient, *k*, of the Ag–SiO<sub>2</sub> films for selected  $t_{Ag-SiO_2}$ . (c) Comparison of percent transmission from UV–vis–NIR measurements (solid lines) and spectroscopic ellipsometry modeled responses (dash) using derived *n* and *k*. For comparison, Figure 4 shows the chromaticity coordinates of the Ag–SiO<sub>2</sub> films from 15 to 90 s evaluated in transmission. The optical properties of a representative bulk Ag film are shown for comparison to our Ag–SiO<sub>2</sub> films in (a,b).<sup>48</sup> Reproduced with permission from 230408-003333. Copyright 1991 Academic Press.

 $2.6 \times 10^{-5} \Omega$  cm for  $t_{Ag-SiO_2} = 90$  s as Ag coalescence increased within the film (compare Figure 2 and the increase in *k* in Figure 5b). The derived differences in resistivity correspond to increases in the derived scattering time ( $\tau$ , in units of femtoseconds, fs) on the order of 0.26 fs for  $t_{Ag-SiO_2} = 60$  s and 4.51 fs for  $t_{Ag-SiO_2} = 90$  s. Obtained from the J.A. Woollam CompleteEASE materials database, Figure 5a,b shows the optical properties of a representative fully coalesced bulk Ag film from Palik that was parameterized using a general oscillator layer for comparison with our Ag–SiO<sub>2</sub> films.<sup>48</sup>

To empirically confirm the goodness-of-fit for these derived optical constants in the depicted wavelength range, we modeled the transmission of the representative Ag-SiO<sub>2</sub> films using Essential Macleod optical coating design software (v. 11.7.599) and compared with the experimental spectra from Figure 3. This optical coating design software package uses conventional transfer matrix modeling of incident plane waves to predict thin-film optical responses based on the input n and k data derived from spectroscopic ellipsometry. Shown in Figure 5c, example transmission spectra from the modeled optical designs represent the three-layer SiO<sub>2</sub>/Ag-SiO<sub>2</sub>/SiO<sub>2</sub> coating with the correspondingly derived n and k from the ellipsometry data analysis (as discussed) at the respective  $t_{Ag-SiO_2}$  (i.e., d from the XRR analysis in Table 2) on top of a fused silica substrate (0.87 mm thick). The modeled transmission responses (dashed lines) shown in Figure 5c agree with the experimental transmission from UV-vis-NIR spectrophotometry measurements (colored solid lines). This comparison further validates our simplistic optical dispersion data analysis approach of the spectroscopic ellipsometry data. The simplicity of this modeling approach is appealing as an effective medium approximation was not employed. The agreement between experimental and modeled transmission responses is likely due, in part, to the ultrathin thickness of these films (constrained by known d from XRR) and dominating absorptive anomalous optical dispersion behavior from the  $\Psi$  and  $\Delta$  data appended with transmission intensity spectra. Although we omitted effective medium approximation parameterization in our optical dispersion data analysis (consistent with complementary metal-dielectric thin-film studies to date),<sup>2,39</sup> we note that our derived optical properties still resemble effective dispersion values, given the composite nature of these films (dependent on  $t_{Ag-SiO_2}$  discussed throughout). While omitted in our analysis, we further note the potential need for such effective medium mixing model considerations in future work that may comprise more complex ultrathin-film configurations or during in situ film growth mechanistic studies. Overall, these data illustrate the wide range of optical property control from co-sputtered Ag-SiO<sub>2</sub> films at ultrathin thicknesses (i.e., representative maximum  $\Delta n = 3.8$  and  $\Delta k = 9.4$  at film thickness  $\leq 10$ nm). Subsequently, this offers a significant range in the pending design and development of precision complex index optical coatings and optoelectronic multilayer devices with integrated ultrathin-film heterogeneous metal-dielectric layers.

### 4. CONCLUSIONS

The optical properties of our ultrathin Ag–SiO<sub>2</sub> nanocomposite films  $\lesssim 10$  nm in thickness have been shown to change under controlled magnetron co-sputtering conditions at ambient substrate temperature. The process control we illustrate in this work results in a structural transition of embedded Ag nanoparticles to contiguous partially coalesced Ag networks in a SiO<sub>2</sub> matrix. The change in Ag morphology is made possible by the controlled inclusion of low-percent composition co-sputtered SiO<sub>2</sub> as a function of increasing  $t_{Ag-SiO_2}$  and Ag coalescence. The resulting structural changes yield tailored light-matter interactions observed from optical intensity measurements (transmission, reflectance, and absorptance) and derived from spectroscopic ellipsometry data analysis (n and k). The measured and modeled percent transmission spectra show good agreement, where modeled transmission is determined using the derived n and k from variable-angle spectroscopic ellipsometry. In the visible wavelength region, absorptance peaks shifted from 430 to 510 nm, and the width of the absorptance peaks are also shown to broaden as  $t_{Ag-SiO_2}$  increased (i.e., 15–40 s). The absorptance was shown to increase at longer wavelengths upon increasing  $t_{Ag-SiO_2} = 60-90$  s. This corresponds to the partially coalesced Ag network throughout the SiO<sub>2</sub> matrix and begins to resemble more bulk-like Ag characteristics (density, resistivity, and optical properties). Such ultrathin-film control reported in this work is largely unobserved for homogeneous thin-metal films and presents greater accessibility toward the integration of ultrathin-film metal composite layers within next-generation multilayer high-precision optical coatings and optoelectronic devices. Future work is expected to further elucidate the range of plasmonic heterogeneous metal-dielectric nanocomposite coating process control and the resulting manipulation of optical behavior in the deposition and design of highperformance optical coating media including precision filters and mirrors.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.3c00853.

Film density and thickness plot, XRR patterns, XRR layer analysis, XPS high-energy resolution spectra, and spectroscopic ellipsometry fit parameters (PDF)

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported by the Materials and Manufacturing Directorate within the U.S. Air Force Research Laboratory (AFRL) via contract number FA8650-16-D-5404-0013. The authors thank Dr. Kurt G. Eyink (AFRL) for discussions involving the optical dispersion data analysis of spectroscopic ellipsometry measurements.

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