A comprehensive analysis of the contributions to the nonlinear optical properties of thin Ag films

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The nonlinear optical properties of 20 nm thick Ag films are investigated by time-resolved white-light continuum pump-probe experiments in both transmission and reflection mode. The dynamics of changes in permittivity $\Delta \varepsilon$ are measured at wavelengths between 500 to 700 nm. The data is fitted to a modified Drude model in the frequency domain and to a two-temperature model in the time domain. Changes in the individual Drude parameters are calculated as a function of time. A single, coherent model is proposed based on these fittings that describes the dynamics of the nonlinear optical properties of Ag, which could be used to model the nonlinear responses of multilayer structures containing thin films of Ag. The physical origins of the observed responses are discussed.


I. INTRODUCTION

The nonlinear optical properties of noble metals have received great attention because the nonlinearity is orders of magnitude larger than in any other known material.1–3 Silver in particular is interesting because the interband absorption peaks lie energetically above the visible spectrum, opening up the possibility of broadband applications in the visible portion of the spectrum.4–8 The electronic and thermal properties that contribute to the nonlinearity, however, are not straightforward, and no fewer than five different processes contribute. These include both interband and intraband (free-electron) contributions, each of which include electron temperature and lattice temperature dependent components. All of these contributions are different from the relatively weak pure $\chi^{(3)}$ processes [on the order of $2 \times 10^{-11}$ esu measured by third-harmonic generation at 1064 nm (Ref. 9)]. Understanding the source and nature of these contributions is essential to maximizing the effects of these nonlinear processes in more complex structures such as metal-dielectric photonic crystals14,15,11 or induced transmission filters.12,13

A number of experimental investigations involving the steady state thermo-optic properties of Ag were carried-out in the 1970s that focused on both the temperature-independent,14–16 and temperature-dependent17–21 optical properties. In these experiments the optical properties were probed by transmission or reflection spectroscopy, by ellipsometry, or by some combination thereof. These experiments combined with concurrent theoretical work provided good insight into how the inherent film structure affects the optical properties.15,16,22,23 how the interband absorption spectrum is expected to change with temperature,17–19 and what role electron-electron interactions might play.14,20 However, these experiments were limited in that they were unable to distinguish effects that depend on the electron temperature from those that depend on the lattice temperature. Also, the dynamics of electron-electron and electron-phonon interactions could not be captured because these experiments were carried-out at steady state.

In more recent years, a number of femtosecond (fs) pump-probe experiments have been performed on thin silver films in order to measure the dynamics of the electrons.24–29 Such experiments are difficult to perform because the thickness of the Ag film that can be measured for optical nonlinearity is limited by its reflectance and absorbance to less than 40 nm. However, the measurements that have been made give insight into the electron behavior, from the initially excited athermal electron distribution25,26 to the rate of electron-phonon interaction24 and the relative strengths of the interband and intraband contributions.27 Investigations have also been made into the frequency dependent changes in the neighborhood of the interband transitions in the near UV (Ref. 28) and in the intraband contributions in the visible.29 Still, it is difficult to attribute with certainty the physical origin of all of the observed nonlinear behaviors and precise quantitative measurements of the intraband contributions are lacking. With the present experiments we discuss current understanding of the origin of the nonlinear optical response of Ag while at the same time providing a simple model that can be used to predict this response when thin Ag layers, like the ones described in this paper, are incorporated into more complex multilayer structures.

The physical mechanisms that contribute to the nonlinear properties of Ag have, in general, different temporal and/or spectral contributions to either the real or imaginary part of the dielectric permittivity $\varepsilon$, so, in theory it should be possible to distinguish among these contributions from a single set of measurements provided they cover sufficiently large spectral and temporal ranges. To this end, we have
performed fs white-light continuum (WLC) pump-probe spectroscopy in both transmission and reflection modes on a thin (20 nm) film of Ag. From these measurements, with full knowledge of the structure, we determined \( \varepsilon \) across the spectral range of the white light continuum probe for times both during and after the interaction of the pump with the sample. Then we fit \( \varepsilon \) using a two temperature model in the time domain and a modified Drude model in the frequency domain. The Drude model was modified to take into account a main. The Drude model was modified to take into account a origin of each nonlinear contribution.

The rest of the paper is organized as follows: Sec. II describes the experimental methods used to fabricate and characterize the linear and nonlinear properties of Ag films; Sec. III gives the results of the measurements; and Sec. IV presents a discussion of the results, including the physical origin of each nonlinear contribution.

II. EXPERIMENTAL METHODS

A. Fabrication

All samples were fabricated on 0.16 mm thick glass cover slips that had been cleaned ultrasonically in soap, deionized water, acetone, and isopropanol for 15 min each. The films were deposited with a Kurt J. Lesker Axxis electron beam deposition system with a starting pressure of 1.3 \( \times 10^{-6} \) Pa. The Ag and SiO\(_2\) layers were deposited at a rate of 0.2 nm/s and the Ti layers at a rate less than than 0.02 nm/s, controlled manually in order to achieve subnanometer thickness. The samples were actively cooled and held at room temperature throughout the deposition. A “bulk” 0.16 mm thick Ag film was deposited as a reference sample. The samples to be measured for optical nonlinearity consisted of 20 nm thick layers of Ag covered by 50 nm thick layers of SiO\(_2\), with a 0.25 nm thick Ti layer before and after the Ag to improve adhesion.

B. Linear optical characterization

The linear optical properties of the samples were measured using a combination of spectroscopic ellipsometry, transmittance, and reflectance measurements. Ellipsometric measurements were made using a Woollam M2000 spectroscopic ellipsometer and transmission measurements were made using a Cary 5E UV/Vis/NIR spectrophotometer. Reflection measurements were made using a xenon light source and a monochromator; detection was accomplished by a pair of Si photodiodes for signal and reference that were connected to lock-in amplifiers. The standard sample used for reflection measurements was a 160 nm thick Ag film covered by 50 nm of SiO\(_2\). The measurements were corrected to account for the fact that the reflectance of the standard is not exactly 100% but closer to 98%. The correction factor was calculated using the matrix transfer method applied to this structure, assuming a bulk refractive index for Ag. This resulted in the reflection data being adjusted upward by 1%–2% across the visible spectrum.

The permittivity of the thick Ag film was measured by spectroscopic ellipsometry. Typically, for a thin film of absorbing material, it is not possible to determine the complex permittivity and the thickness simultaneously using ellipsometry; however, since this film is thick enough to be fully opaque, the thickness is irrelevant and the complex permittivity can be fully determined.

The 20 nm thick Ag film is not fully opaque, so the permittivity cannot be uniquely determined using ellipsometry. For this reason, the permittivity was calculated from transmission and reflection data instead. The permittivity was fitted using an iterative numerical fitting routine based on the Newton–Raphson method in which the matrix transfer method was used to calculate the transmittance and reflectance of the structure. The starting point for the fitting routine was the measured bulk permittivity of Ag and, with each iteration, the permittivity was adjusted to minimize the discrepancy between the model and the measured data. In only a few iterations it was possible to match the model to within less than the measurement error. This point by point fitting routine was repeated independently for each wavelength.

C. WLC pump-probe spectroscopy

The nonlinear optical properties were probed using a commercially available pump-probe spectroscopy system (Helios, Ultrafast Systems). A portion (~5%) of a laser beam from a Ti:sapphire regenerative amplifier (Spectra-Physics) operating at 800 nm and 1 kHz repetition rate provided the probe pulse to generate a WLC (WLC, 500–700 nm) while the remainder of the beam generated the pump pulse, tuned to either 550 or 650 nm by an optical parametric amplifier (TOPAS-White, Spectra-Physics). The pump beam was chopped at 500 Hz with a 50% duty cycle, with reference spectra being measured while the pump beam was blocked. The signal and reference data were averaged over a thousand measurements at each probe time delay, and a \( \Delta OD \) spectrum was generated. The result was a wavelength versus time two-dimensional array of \( \Delta OD \) values. The transmission mode measurements were converted to \( \Delta T \) values based on the measured linear transmittance \( T \) according to

\[
\Delta T = T(10^{-\Delta OD} - 1).
\]

The process was repeated for reflection mode. The size of the pump beam at focus was measured using a knife-edge scan and yielded values of 260 \( \mu \)m (1/e radius) at 650 nm, 234 \( \mu \)m (1/e radius) at 550 nm, and the probe beam was 60 \( \mu \)m (1/e radius). Because the probe is significantly smaller than the pump, it is assumed that the probe overlaps with a region of constant (peak) fluence from the pump. A chirp correction factor was calculated by measuring the cross phase modulation response in the substrate, and the scattered pump light was subtracted based on measurements where the probe preceded the pump so that there was no observable nonlinear response of Ag. The pump pulse duration was 60 fs and the total instrument response time was 150 fs, precluding the possibility of investigating the initial athermal electronic behavior. For this reason, this work focused on time delays...
larger than 1 ps, at which point the electrons are expected to have reached a thermal distribution.

III. EXPERIMENTAL RESULTS

A. Linear characterization

It is well known that the permittivity of Ag is dependent upon the deposition conditions,\textsuperscript{16,31,32} thus, it is necessary to characterize each film individually. The frequency dependence of the permittivity in the visible region of the spectrum can generally be described by the Drude model

\[ \varepsilon = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \]

where \( \varepsilon_{\infty} \) is the sum of the interband contributions, \( \omega_p \) is the bulk plasma frequency, and \( \gamma \) is a damping constant. Equation (2) can be decomposed into its real and imaginary components, assuming \( \gamma \ll \omega \)

\[ \varepsilon_r = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2}, \quad \varepsilon_i = \frac{\gamma\omega_p^2}{\omega^2}, \]

where \( \gamma \) can be separated into a frequency independent term \( \gamma_t \) and a frequency dependent term \( \beta \)

\[ \gamma = \gamma_t + \beta\omega^2. \] (4)

Strictly speaking, \( \varepsilon_{\infty} \) is a function of frequency. Its dispersion could be calculated using the Kramers–König relation from the interband absorption spectrum, though such calculations are beyond the scope of this paper and \( \varepsilon_{\infty} \) is approximated as a constant. This dispersion makes it difficult to fully separate the contributions of \( \varepsilon_{\infty} \) and \( \omega_p \) to \( \varepsilon_r \), as will be seen below.

The three temperature independent factors that most strongly affect the permittivity in the visible region of the spectrum are the density (void fraction) of the film,\textsuperscript{15} the grain size,\textsuperscript{15,16} and surface roughness.\textsuperscript{14,16} The density governs the strength of the interband absorption and bulk plasma frequency \( \omega_p \), and the other two affect the free-electron damping parameter \( \gamma \). Film thickness plays a significant role; the thinner the film, the more important surface roughness becomes.

The measured dispersion of the permittivity of the 160 nm thick Ag film is shown in Fig. 1. The permittivity was fitted to the Drude model with \( \varepsilon_{\infty}=4, \omega_p=1.38 \times 10^{16} \text{ s}^{-1}, \gamma_t=2.73 \times 10^{13} \text{ s}^{-1}, \) and \( \beta=5.9 \times 10^{-18} \text{ s}^{-1}. \) These numbers compare favorably with values from the literature \( \omega_p=1.36 \times 10^{16} \text{ s}^{-1}, \gamma_t=2.73 \times 10^{13} \text{ s}^{-1}, \) and \( \beta=5.8 \times 10^{-18} \text{ s}^{-1}; \textsuperscript{20,33} \) \( \varepsilon_{\infty} \) differs significantly from the values of 2.7–3.4 reported in Refs. 14 and 20 though it agrees well with the value of 4 reported in Ref. 16. The variations in this value can be attributed in part to varying densities of the Ag films and to experimental errors either in the present measurements or the cited values; it should be noted that none of these measurements take into account dispersion in \( \varepsilon_{\infty}. \)

It was shown in Ref. 16 that, in bulk Ag, if the grain size is smaller than the intrinsic mean free path (\( \sim 52 \text{ nm} \)), then \( \gamma \) will increase linearly with the inverse of the grain diameter. This arises from the fact that grain boundaries interrupt the free-flow of electrons, so the mean free path is limited by the diameter of the grains. The present value of \( \gamma \) is very close to the damping value of \( 2.6 \times 10^{13} \text{ s}^{-1} \) that would be expected from a large, perfect crystal of Ag, indicating that the grain size is on the order of 50 nm or more.

The bulk plasma frequency \( \omega_p \) is defined as

\[ \omega_p = \left( \frac{4\pi Ne^2}{m^*} \right)^{1/2}, \] (5)

where \( N \) is the density of free carriers, \( e \) is the electron charge, and \( m^* \) is the effective electron mass. Because \( \omega_p \) is a function of carrier density, its value can be used to estimate the void fraction in the film. In view of Fig. 4 of Ref. 16, which plots the relationship between the void fraction and \( \omega_p \), it can be seen that the present film is essentially void free.

The permittivity and thickness values of the thin film that were to be used in the analysis of the optical nonlinearity measurements were calculated from transmittance and reflectance measurements shown in Fig. 2 by using the same fitting process as described above. The thickness was determined to be 19.7 nm and the permittivity was fitted to the Drude model with parameters identical to the bulk film except with \( \gamma_t=8 \times 10^{13} \text{ s}^{-1} \). This difference is due either to increased surface scattering in the thinner film or a smaller grain size. The complex permittivity is shown in Fig. 1. These values form the basis of the nonlinear characterization of these films by pump-probe spectroscopy.
dependent electron specific heat, \( T_e \)

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where \( \omega_p \) and \( \gamma \) to vary with electron and lattice temperature. This was accomplished in

FIG. 3. (Color online) Evolution of (a) transmittance, (b) reflectance, (c) real part of permittivity, and (d) imaginary part of permittivity of 20 nm thick Ag film from 0.5 ps to 5 ps after 50 J/m² pulse.

B. WLC pump-probe spectroscopy

WLC pump-probe measurements were carried out with incident fluences of 50, 37.5, 25, and 12.5 J/m² at a pump wavelength of 650 nm and 68 J/m² at 550 nm. Figure 3 shows the evolution of the nonlinear transmission and reflection of the 19.7 nm thick Ag film with a pump wavelength of 650 nm and a fluence of 50 J/m², starting at a delay of 0.5 ps and ending at a delay of 5 ps. The corresponding evolution of the 19.7 nm thick Ag film with a pump wavelength of 650 nm and a fluence of 50 J/m², starting at a delay of 0.5 ps and ending at a delay of 5 ps. The corresponding evolution of the nonlinear transmission and reflection of the 19.7 nm thick Ag film with a pump wavelength of 650 nm and a fluence of 50 J/m², starting at a delay of 0.5 ps and ending at a delay of 5 ps.

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FIG. 4. (Color online) Evolution of electron and lattice temperatures of 20 nm thick Ag film calculated by the two temperature model for pump fluences 50, 37.5, 25, and 12.5 J/m² (semilog scale).
two stages. First, the response due to the electron temperature was extracted from the measurements in the neighborhood of 1 ps delay, at which time the change in electron temperature is near its maximum and the change in lattice temperature is still small. Second, the response due to the lattice temperature was extracted from the measurements after 6 ps, when the electrons have reached thermal equilibrium with the lattice, as shown in Fig. 4.

The response of $\varepsilon_r$ is treated here first. At both time scales the response of $\varepsilon_r$ was determined to be due primarily to the temperature dependence of $\gamma$, which can be described as

$$
\gamma_1[T_i(t), T_e(t)] = 5.12 \times 10^{13} + (8.5 \pm 1.0) \times 10^{10} T_i(t) + (3.0 \pm 0.2) \times 10^6 T_e^2(t). 
$$

(7)

The interband contribution to $\varepsilon_r$ that has been investigated in depth in other studies does not contribute to the present measurements because the interband contribution is highly localized around the interband transition frequencies, outside the range of the present measurements.

The response of $\varepsilon_r$ is more complex because it involves contributions from both $\varepsilon_\infty$ and $\omega_p$. First, $\omega_p$ was assumed to be independent of electron temperature, so the response at 1 ps could be attributed solely to changes in $\varepsilon_\infty$. This is physically reasonable because changes in $\varepsilon_\infty$ should mainly arise from interband contributions while changes in $\omega_p$ could arise from effects such as band shifting that are more closely related to changes in the lattice temperature. Due to the Kramers–Krönig relation, changes in $\varepsilon_r$ induce a spectral dispersion in $\varepsilon_r$ that cannot be reproduced by assuming that $\varepsilon_\infty$ is frequency independent. Including the exact contributions of the different interband transitions would add additional complexity to the model and is out of the scope of this paper. Instead a frequency dependent term is introduced

$$
\varepsilon_\infty[\omega, T_e(t)] = 4 + [3.0 \pm 0.2] \times 10^{-8} + (1.3 \pm 0.1) \times 10^{39} \omega^2 \times T_e^2(t),
$$

(8)

The frequency dependent term is in the form of a two-term Cauchy equation. This dispersion depends strongly on the fact that there is no electron temperature dependent component of $\omega_p$; if such dependence exists, this dispersion will change significantly.

After 6 ps, changes in $\varepsilon_\infty$ and $\omega_p$, both contribute to the response of $\varepsilon_r$. Since both terms have a frequency dependence, it is difficult to distinguish between the two. However, there seem to be two different origins to changes in $\varepsilon_r$ because the response changes from positive to negative at about 5 ps and because the response is stronger at lower frequencies after this point. Thus, it seems clear that changes in $\varepsilon_\infty$ are not enough to explain the observed response of $\varepsilon_r$.

In order to place bounds on the relative magnitudes of the contributions of $\varepsilon_\infty$ and $\omega_p$, it was assumed that the slope of the dispersion of $\varepsilon_r$ due to the change in lattice temperature would be greater than zero and within a factor of two of the dispersion due to electron temperature. The measured frequency dependence of $\varepsilon_r$ was then fitted with $\varepsilon_\infty$ and $\omega_p$. If $\varepsilon_\infty$ is assumed to be dispersionless, the resulting expressions are

$$
\varepsilon_\infty[T_i(t)] = 3.94 + (1.7 \pm 1.2) \times 10^{-4} T_i(t),
$$

(9a)

$$
\omega_p[T_i(t)] = 1.374 \times 10^{16} + (1.8 \pm 0.5) \times 10^{11} T_i(t). 
$$

(9b)

If, on the other hand, the slope of the dispersion of $\varepsilon_r$ is assumed to be double that of the electron temperature dependence, the resulting expressions are

$$
\varepsilon_\infty[\omega, T_i(t)] = 3.94 + (0.4 \pm 0.6 \times 10^{-32} \omega^2) \times (1.5 \pm 1.0) \times 10^{-4} T_i(t),
$$

(10a)

$$
\omega_p[T_i(t)] = 1.374 \times 10^{16} + (1.6 \pm 0.4) \times 10^{11} T_i(t),
$$

(10b)

where the dispersion term in $\varepsilon_\infty$ was chosen so that its magnitude would be 1 in the center of the frequency range, so that the magnitudes of the dispersive and nondispersive temperature dependences can be directly compared. As expected, the uncertainty in these equations is quite large. However, it is apparent that uncertainty in the degree of dispersion in $\varepsilon_\infty$ is less a contributing factor than the uncertainty in the measurements themselves. This is due to the fact that changes in $\omega_p$ appear to have a greater contribution to the nonlinear response than changes in $\varepsilon_\infty$ after the electrons and lattice have reached thermal equilibrium. The dominance of $\omega_p$ also explains why there is a sign change in $\Delta \varepsilon_r$.

The constant terms in Eqs. (8), (9a), (9b), (10a), and (10b) were set so that at room temperature ($T_i = T_e = 300$ K) the Drude parameters would have the values $\varepsilon_\infty = 4$ and $\omega_p = 1.38 \times 10^{16}$ s$^{-1}$ taken from the linear characterization measurements in the preceding section.

Equations (7), (8), (9a), (9b), (10a), and (10b) can be combined into a single set of equations to describe the full nonlinear response in terms of electron and lattice temperatures

$$
\varepsilon_\infty[\omega, T_i(t), T_e(t)] = 3.94 + (0.7 \pm 3.0 \times 10^{-32} \omega^2) \times [(1.5 \pm 1.0) \times 10^{-4} T_i(t) + (4.3 \pm 0.5) \times 10^{-8} T_e^2(t)],
$$

(11a)

$$
\omega_p[T_i(t)] = 1.374 \times 10^{16} + (1.6 \pm 0.4) \times 10^{11} T_i(t),
$$

(11b)

$$
\gamma_1[T_i(t), T_e(t)] = 5.12 \times 10^{13} + (8.5 \pm 1.0) \times 10^{10} T_i(t) + (3.0 \pm 0.2) \times 10^6 T_e^2(t),
$$

(11c)

where, for $\varepsilon_\infty$, the dispersion of the $T_i$ term is assumed to be equal to the dispersion of the $T_e$ term.

The temporal evolution of these parameters can be seen in Fig. 5 for a pump fluence of $50 \text{ J/m}^2$. As shown in Fig. 6, these equations describe the changes well in both the time and frequency domains for all pump fluences at both pump frequencies. This consistency confirms the fact that the observed effects are purely thermal in character. Hence, though there is some uncertainty in the exact magnitudes of the individual contributions, this set of equations can be used to describe the nonlinear optical response of a thin Ag film. As
such, this model is useful for designing more complex multilayer structures incorporating this nonlinear optical response.

Further discussion of the nature and physical cause of each of these effects follows in Sec. III.

IV. DISCUSSION

There are at least five distinct contributions to the nonlinear response of a thin Ag film; these contributions correspond to the five temperature dependent terms found in Eq. (11). Figure 7 illustrates, using the model of a 50 J/m² pump pulse at 650 nm, how each of these terms contributes uniquely to the observed changes in the complex permittivity.

First, Figs. 7(a) and 7(b) show the distinction between the contributions to the permittivity that are dependent on the lattice temperature $T_l(t)$ and those dependent on the electron temperature $T_e(t)$. The change in permittivity was calculated as follows. First, $T_l(t)$ and $T_e(t)$ were calculated from the TTM (corresponding to the top curves of Fig. 4). From these, the Drude parameters were calculated using Eq. (11). For instance, $e_{rr}[\omega, T_e(t), T_l=300]$ was used to isolate the lattice temperature dependent contribution of $e_{rr}$, and $e_{rr}[\omega, T_l=300, T_e(t)]$ was used to isolate the electron temperature dependence. The other two Drude parameters, $\omega_p$ and $\gamma_l$, were calculated similarly. The Drude parameters were then inserted into Eq. (3) to calculate the change in complex permittivity over time. It can be seen that before thermal equilibrium is reached the high temperature of the electron cloud produces a large effect but after equilibrium the lattice contribution is dominant.

Figures 7(c) and 7(d) show the contributions of each of the Drude parameters to $e_{rs}$ and $e_{s}$ 10 ps, after thermal equilibrium between the lattice and electron cloud has been reached. Figure 7(c) shows that the contribution due to $\omega_p$ is dominant over that of $e_{rs}$ in the response of $e_{rs}$, as was described earlier. Figure 7(d) shows that, while there is some slight contribution of $\omega_p$ to the response of $e_{s}$, it is negligibly small. Thus, the assumption that the nonlinear response of $e_{s}$ can be calculated solely based on changes in $\gamma$ is justified.

The physical cause of each contribution is now discussed in turn.

A. Interband effects

In the interband regime the behavior is typically attributed to three transitions. Two transitions, namely from the $d$-band to the $p$-band and from the $p$-band to the $s$-band, occur near the $L$ point in the Brillouin zone, the third transition is near the $X$ point. All of these transitions fall well inside the ultraviolet spectrum, so for applications in the visible spectrum the only observable effect is via the Kramers–Kronig relation. This is the $e_{rr}$ term of $e_{rr}$.

Several different temperature dependent interband effects contribute to the observed optical properties. The first is Fermi smearing, in which the distribution of electron energies around the Fermi energy is spread out. This leads to a broadening of the absorption band with increasing...
temperature and an increase in the value of $\varepsilon_{\infty}$. It has been shown⁻ that the change in permittivity is proportional to the total energy contained in the electron cloud. An important distinction is that the energy is not directly proportional to the electron temperature because the electron specific heat is itself a function of temperature. Neglecting the electron-lattice coupling in Eq. (6a) and integrating gives

$$\frac{65 T_e^2}{2} = E_e,$$

where $E_e$ is the total thermal energy contained in the electron cloud. In terms of temperature, then, Fermi smearing follows $T_e^2$, as can be seen in Eq. (11a).

The second interband effect is band shifting, which is caused by thermal expansion in the silver crystals and follows the lattice temperature. As the crystals heat up and expand, the energy levels of the valence and conduction bands, as well as the Fermi energy, shift. This leads to a corresponding shift in the absorption spectrum, which can again be observed in $E_{\infty}$ through the Kramers–Kronig relationship. The specific heat of the lattice is constant within this temperature range, so it is expected that this effect follows $T_l$; this again can be seen in Eq. (11a).

Other effects, such as those listed in Ref. 36 may contribute to the interband nonlinear response but in this wavelength range their effects cannot be separated from Fermi smearing and band shifting for the present set of measurements.

### B. Intraband effects

The intraband regime is described by the Drude model, as shown above, with temperature dependent parameters $\gamma$ and $\omega_p$.

At least three mechanisms, electron-phonon scattering, electron-electron scattering, and electron-surface scattering contribute to $\gamma$. Electron-phonon scattering is the mechanism by which energy is transferred between electrons and the lattice and vice versa, and is the largest contribution to damping at room temperature. The scattering rate is proportional to the lattice temperature $T_l$ due to an increase in the number of phonons. Holstein’s expression for the temperature dependence of electron-phonon interaction $\gamma$ is

$$\gamma_{\text{e-ph}} = \frac{\gamma_0}{2} \left[ 5 + 4 \left( \frac{T_l}{\Theta} \right)^5 \int_0^{\Theta/T_l} \frac{z^4dz}{e^z - 1} \right],$$

where $\Theta=220$ K is the Debye temperature. For $T_l > \Theta$, this equation can be approximated well by a linear function of $T_l$.

$$\gamma_{\text{e-ph}} = \gamma_0 \left( 7.5 \times 10^{-2} + 4.43 \times 10^{-2} T_l \right).$$

The value for $\gamma_0$ can be extracted from the Drude parameters of bulk Ag, in the thermal range where the electron-electron contributions are negligible. As stated previously, $\gamma_i = 2.73 \times 10^{13} $ s$^{-1}$ for our bulk film, so $\gamma_0 = 1.94 \times 10^{13} $ s$^{-1}$. Assuming that this value holds for the 19.7 nm thick film as well, then $\Delta \gamma_i / \Delta T_l = 8.6 \times 10^{10} $ s$^{-1}$ K$^{-1}$. This matches well with the calculated value of $8.7 \times 10^{10} $ s$^{-1}$ K$^{-1}$ from Eq. (11c).

Electron-electron scattering is expected to have a thermal dependence based on $T_e^2$ (Ref. 14)

$$\gamma_{\text{ee}} = \frac{1}{12} \pi^3 \Gamma \Delta(1/hE_F)[(k_B T_e)^2 + (h\omega/2\pi)^2],$$

where $\Gamma=0.55$ is the average of the scattering probability over the Fermi surface, $\Delta=0.75$ is the fractional Umklapp scattering, and $E_F=5.5$ eV is the Fermi energy. Typically, the temperature dependent term is neglected because it does not become significant until $T_e > 1000$; since this threshold is exceeded in the present system, this temperature dependence must be considered. It follows from Eq. (15) that $\Delta \gamma / \Delta T_e^2 = 2.2 \times 10^6 $ s$^{-1}$ K$^{-2}$, compared to $2.9 \times 10^6 $ s$^{-1}$ K$^{-2}$ from Eq. (11c). A surface scattering contribution may in part make up some of this discrepancy; it would require taking a series of measurements on samples with carefully controlled surface morphologies to verify this.

Surface scattering results from diffuse reflection of electrons off the surface of the film; the strength of this contribution is morphology and thickness dependent, affected particularly by the surface roughness. This accounts for a large part of the difference in $\gamma$ between the bulk Ag film and the thin Ag film; however, the nonlinear contribution is unclear.

The thermal dependence of $\omega_p$ is not a well documented phenomenon because it is difficult to distinguish from other thermal effects, as stated earlier. Different values have been reported at different temperatures, but the precision has been low. Variations in $\omega_p$ have been attributed as the cause of certain “ringing” phenomena in nanoparticles, but it is difficult to quantify the effect from such experiments. Considering Eq. (5), there are two possible explanations for the variation: a change in carrier concentration and a change in electronic effective mass. Considering the thermal expansion of Ag, the carrier concentration might be expected to decrease with increasing lattice temperature. However, only an increase in $\omega_p$ is observed in the present experiments so this is not a sufficient explanation. It is possible that as the band structure changes the effective mass is also modified; the precise determination of the causes of this effect will require further experiments and is beyond the scope of this paper.

The contributions to the nonlinear response of Ag can be categorized in several different ways: (1) whether it arises from interband or intraband effects; (2) whether it is electron temperature or lattice temperature dependent; and (3) whether the observed change occurs predominantly in the real or imaginary permittivity. Table I gives a summary of the nature of each contribution.

<table>
<thead>
<tr>
<th>Source</th>
<th>Drude parameter</th>
<th>Interband/Intraband</th>
<th>Electron/Lattice</th>
<th>Effect observed in $\varepsilon_r$/$\varepsilon_{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermi smearing</td>
<td>$\varepsilon_{\infty}$</td>
<td>Interband</td>
<td>Electron</td>
<td>$\varepsilon_r$</td>
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<td>Band shifting</td>
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<td>Electron-phonon</td>
<td>$\gamma_i$</td>
<td>Intraband</td>
<td>Lattice</td>
<td>$\varepsilon_i$</td>
</tr>
<tr>
<td>Electron-electron</td>
<td>$\gamma_i$</td>
<td>Intraband</td>
<td>Electron</td>
<td>$\varepsilon_i$</td>
</tr>
<tr>
<td>Plasma frequency</td>
<td>$\omega_p$</td>
<td>Intraband</td>
<td>Lattice</td>
<td>$\varepsilon_i$</td>
</tr>
</tbody>
</table>

$\gamma_{\text{ee}} = \frac{1}{12} \pi^3 \Gamma \Delta(1/hE_F)[(k_B T_e)^2 + (h\omega/2\pi)^2],$
V. CONCLUSION

The WLC pump-probe measurements presented in this paper were used to identify five different contributions to the nonlinear processes of Ag: Fermi smearing, band shifting, electron-phonon scattering, electron-electron scattering, and changes in bulk plasma frequency. Open questions remain about the contributions of electron-surface scattering and the cause of the shift in the bulk plasma frequency. The model developed based on these measurements describes well the behavior of a semitransparent 20 nm Ag sample under different pump fluences and excitation wavelengths. The results of this analysis will aid in the rigorous design of more complex structures that take advantage of the nonlinear optical properties of Ag, such as one dimensional metal-dielectric photonic crystals or induced transmission filters.

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