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LETTER TO THE EDITOR

Phonon assisted absorption in thin Ag films using surface plasmon–polaritons

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Abstract. DC resistivities and optical dielectric constants have been obtained from thin Ag films for a range of thicknesses as a function of temperature, both before and after annealing. Discrepancies between DC and optical frequency relaxation times at lower temperatures lead to the conclusion that a significant contribution to the residual imaginary dielectric constant results from phonon assisted absorption. The effect of electron scattering on the phonon assisted absorption is also considered.

In a previous paper (Tillin and Sambles 1990a), the temperature dependence of the dielectric constants of thin Ag films were reported and compared with the DC resistivity. An increasing discrepancy with temperature exists between the relaxation times for the two processes (τ_{op} and τ_{DC} respectively). There have been relatively few measurements of the behaviour of the dielectric constants of Ag with temperature (Winsemius *et al* 1976, Merkt and Wissmann 1980, Hollstein *et al* 1977, McKay and Rayne 1976). However, a feature of all these studies is the relatively high residual component of the imaginary dielectric constant (ε_i) observed at helium temperatures, when compared with the residual resistivity and the ratios of these values with the corresponding quantities at room temperature. This has been attributed mostly to electron–surface and defect scattering (Tillin and Sambles 1990a), although a significant contribution is to be expected from the process of phonon assisted absorption (Holstein 1954, McKay and Rayne 1976). This latter process is the subject of this paper, and is now considered in more detail.

At low temperatures electron–phonon scattering is severely inhibited, as the energy available for the generation of phonons is $\sim k_B T$. However, the process of phonon assisted absorption allows an electron in the skin depth of the metal to absorb a photon, and interact with the lattice to emit a phonon. Thus, as the photon energy is $\hbar\omega$, the available energy for phonon generation is $\geqslant k_B T$, and the measured optical absorption is much greater than given by classical theory.

Holstein (1954) derives an expression for the temperature dependent optical relaxation time by applying second-order perturbation theory to the probability of electron

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transition between two one-electron states, and using the result calculates the rate of EM energy transfer to the material system. The resulting expression is

$$\frac{1}{\tau_{op}} = \frac{1}{\tau_{op}^0}\left(\frac{2}{5} + 4\left(\frac{T}{\theta_D}\right)^5 \int_0^{\theta_D/T} \frac{Z^4}{(e^Z - 1)} dZ\right) \tag{1}$$

where the $\frac{2}{5}$ term corresponds to phonon assisted absorption and the temperature dependent term to phonon scattering processes. τ_{op}^0 is a constant for the metal, that cannot be accurately calculated as it depends on the coupling between electrons and phonons, and θ_D is the Debye temperature of the metal. This is similar to the Bloch–Gruniesen relation for the DC resistivity

$$\frac{1}{\tau_{DC}} = \frac{4}{\tau_{DC}^0}\left(\frac{T}{\theta_D}\right)^5 \int_0^{\theta_D/T} \frac{Z^5}{(e^Z - 1)(1 - e^{-Z})} dZ \tag{2}$$

The constant τ_{DC}^0 is only equal to τ_{op}^0 if there is no anisotropy of the relaxation time over the Fermi surface.

At higher temperatures, equations (1) and (2) tend to similar values (depending on the difference between τ_{op}^0 and τ_{DC}^0), whilst at lower temperatures large discrepancies occur. As $T \rightarrow 0$, $\tau_{DC} \rightarrow \infty$ whilst $\tau_{op} \rightarrow 5\tau_{op}^0/2$.

The experiments were performed *in situ* in a UHV chamber with a helium flow cryostat, with the facility for temperature variation between 25 K and 650 K. The base pressure of the system was $\simeq 2 \times 10^{-7}$ Pa during the experiments. Thin films (30 nm $< d <$ 100 nm) of 6 N purity Ag were deposited at a rate of about 0.15 nm s^{-1} onto a quartz prism substrate. Most films were condensed at room temperature, although some depositions were onto a substrate held at a temperature just above the Debye temperature, θ_D (for Ag, $\theta_D \simeq 225$ K), as this has been shown to produce better quality films (Schleminger and Stark 1986, 1987). The films were then annealed by warming to 300 K for up to 5 hours (until no further change in the resistivity with time was recorded).

The dielectric constants ($\varepsilon_r + i\varepsilon_i$) of the samples were obtained using resonant coupling to surface plasmon–polaritons, which are coupled electromagnetic field-charge density oscillations, excited at the surface of a metal film in the Kretschmann geometry (Kretschmann and Raether 1968). Reflectivity versus incidence angle spectra were recorded using a novel focused light attenuated total reflection technique, described in detail elsewhere (Tillin and Sambles 1990b), at a wavelength of 632.8 nm. The resulting data were fitted to theoretical curves generated from Fresnel's equations, using an iterative least squares fitting routine, to yield values for the dielectric constants and the thickness of the metal film. Such results were combined with resistivity measurements for different thickness and 'quality' (different sample morphology) Ag films.

Figure 1 shows a typical SPP resonance, fitted to theoretical prediction from Fresnel's theory, illustrating the excellent agreement that may be obtained between theory and experiment. The results yield values for the dielectric constants and the film thickness. The optical and DC relaxation times were then calculated using the following relationships

$$\frac{1}{\tau_{op}} = \frac{\omega\varepsilon_i}{(1 - \varepsilon_r)} \qquad \frac{1}{\tau_{DC}} = \frac{ne^2\rho}{m^*} \tag{3}$$

where the value n/m^* was taken from McKay and Rayne (1976), calculated using the relation

$$\frac{n}{m^*} = \frac{1}{12\pi^3}\oint_S v_F \, dS$$

The resulting data sets were then compared to equations (1) and (2) in the following

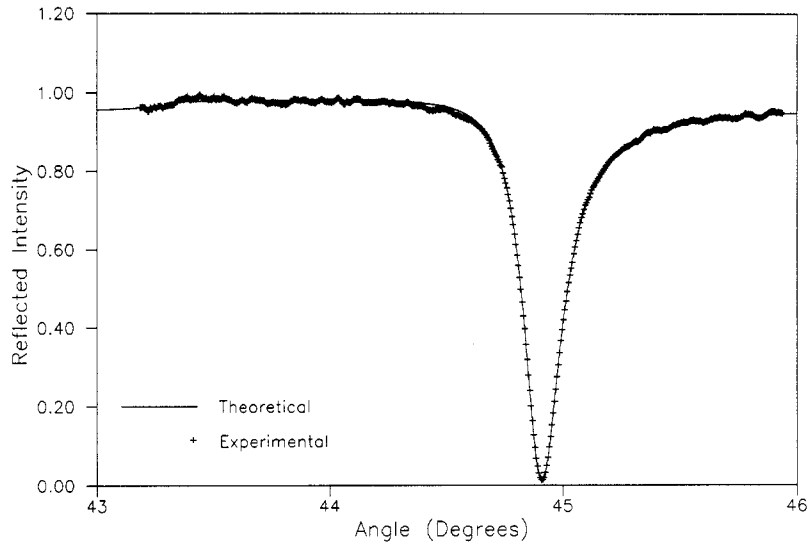

Figure 1. Sample reflectivity versus angle of incidence resonance data for a 52 nm annealed Ag film at 632.8 nm, fitted to the theoretical prediction from Fresnel's theory.

way. A residual ε_i (ε_i^{res}), corresponding to surface and defect scattering, was subtracted from the data and τ_{op} calculated for the remaining contribution. This was then iteratively least squares fitted to equation (1), which yielded values for τ_{op}^0 and ε_i^{res} (and hence ε_i^{paa}—the contribution to ε_i from phonon assisted absorption). In a similar manner, the resistivity was fitted to (2) to give values of τ_{DC}^0.

Figure 2 shows an example of the fitted optical and DC relaxation time data with temperature, again showing the superb experimental agreement with theory.

Considering all the films under study, average values for the constants from the fitting were obtained of

$$\varepsilon_i^{paa} = 0.066 \pm 0.009$$

$$\tau_{op}^0 = (3.76 \pm 0.58) \times 10^{-14}\ \text{s}$$

$$\tau_{DC}^0 = (4.33 \pm 0.51) \times 10^{-14}\ \text{s}.$$

The value of θ_D used in the analysis was estimated to be ~225 K. However Schleminger and Stark (1987) give evidence that the value of θ_D depends strongly on sample thickness with values from 210 K for thin samples, to 260 K for ones approaching bulk thickness. If θ_D was also varied in the fitting procedure (i.e. a completely free fit), then a value of $\theta_D = 225 \pm 5$ K was obtained for the Debye temperature, from both optical and DC results.

Systematically varying θ_D from 210–260 K, whilst fitting the data yielded a range of average values for the fitting variables as

$$\varepsilon_i^{paa} \sim 0.06 \rightarrow 0.09$$

$$\tau_{op}^0 \sim (4.1 \rightarrow 3.2) \times 10^{-14}\ s$$

$$\tau_{DC}^0 \sim (4.6 \rightarrow 3.8) \times 10^{-14}\ \text{s}$$

At intermediate temperatures, the parameters varied linearly with θ_D as is to be expected.

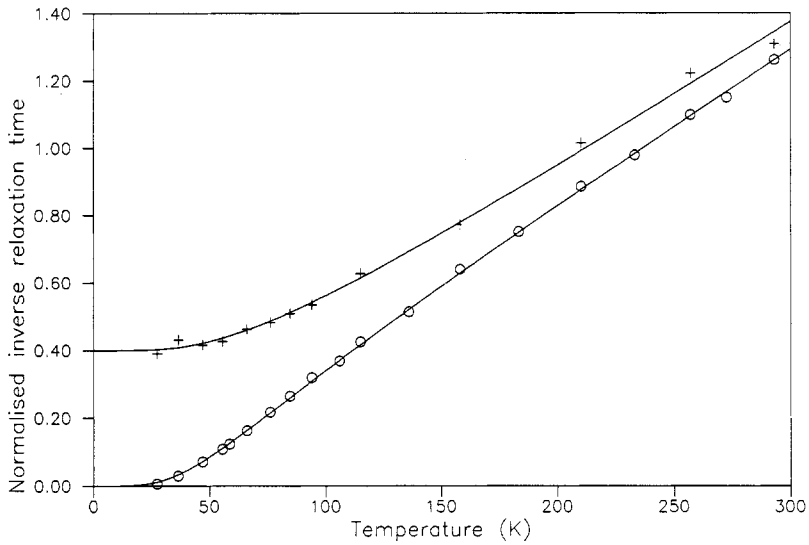

Figure 2. Normalised inverse optical (+) and DC (○) phonon relaxation times, fitted to equations (1) and (2) for the film used to produce figure 1, showing the large discrepancy which exists between the two quantities at low temperatures.

For the lowest defect concentration films measured, $\varepsilon_i^{res} \simeq 0.25$, indicating that ε_i^{paa} forms ~35% of the total residual ε_i at 632.8 nm. On annealing the films, whilst ε_i^{res} significantly decreases, ε_i^{paa} remains unchanged. Consequently, although the value of ε_i^{paa} varies slightly between samples, there is no evidence to suggest that electron–defect and –surface scattering affect the interaction processes of the electrons with phonons, or the lattice, in the process of phonon assisted absorption.

The discrepancy between τ_{op}^0 and τ_{DC}^0 is smaller than observed by McKay and Rayne (1976), the ratio of the two quantities being ~1.13, which is to be compared to their value of nearly 1.35. Whilst their value cannot be attributed to Fermi surface distortion alone, the value of 1.13 obtained above does not seem unreasonable. Mathewson *et al* (1972), observed a 15% enhancement of the optical mass at room temperature, resulting from Fermi surface distortion, similar in magnitude to the effect observed here.

It should be noted that several assumptions are made in the derivation of equation (1). Firstly, that the electrons were effectively free (also assumed in calculating τ_{op} from ε_i for these data), secondly, Umklapp processes were neglected, and finally, a simple Debye model was used for the phonon spectrum. Deviations from these assumptions will yield a value different to the $\frac{2}{5}$ in equation (1). Then although the data could still be fitted to such an expression, slightly different values of ε_i^{paa} and τ_{op} would result, a value lower than $\frac{2}{5}$ giving a reduced ε_i^{paa}. Simultaneous measurements of the resistivity and the first measurement of SPPS observed on cooled Ag films (yielding the dielectric constants of the metal) have shown that a large difference exists between the DC and optical relaxation times at low temperatures. This is explained in the framework of Holstein's model for phonon assisted absorption, a value of $\varepsilon_i^{paa} = 0.066 \pm 0.009$ (the contribution to the residual imaginary dielectric constant) being found for this process. In low defect concentration Ag films at 632.8 nm, this forms about 35% of the total residual ε_i. In addition, differences in the value of τ_{op}^0 and τ_{DC}^0 have indicated ≃10% anisotropy of the relaxation time over the Fermi surface.

References

Hollstein T, Kreibig U and Leis F 1977 *Phys. Status Solidi* b **82** 545
Holstein T 1954 *Phys. Rev.* **96** 535
Kretschmann E and Raether H 1968 *Z. Naturf.* a **23** 2135
Mathewson A G, Aronsson H and Bernland L G 1972 *J. Phys. F: Met. Phys.* **2** L39
McKay J A and Rayne J A 1976 *Phys. Rev.* B **13** 673
Merkt U and Wissmann P 1980 *Surf. Sci.* **96** 529
Schleminger W and Stark D 1986 *Thin Solid Films* **137** 49
—— 1987 *Surf. Sci.* **189/90** 1103
Tillin M D and Sambles J R 1990a *Vacuum* at press
—— 1990b *J. Mod. Opt.* at press
Winsemius P, van Kampen F F, Lengkeek H P and van Went C G 1976 *J. Phys. F: Met. Phys.* **6** 1583