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Reflectance spectra and dielectric functions for Ag in the region of interband transitions

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New measurements have been made of the reflectances of single crystals of Ag and of Ag films in the (3.5—30)-eV range. The data were analyzed with the Kramers-Kronig method and the resultant dielectric functions were compared with those in the literature and with recent calculations. We find all structures previously seen, and a new weak peak at 11.5 eV. Our magnitudes for ϵ_2 are in considerably better agreement with those of the calculated spectra than are those in the literature. Second-derivative spectra of the absorption coefficient have been calculated and compared with previously measured thermotransmission spectra, showing the latter to arise primarily by temperature-dependent broadening.

INTRODUCTION

The optical properties of the noble metals have played an important historical role in our understanding of the optical properties and electronic structures of metals. Despite this, the optical "constants," by which we mean the complex dielectric function, $\tilde{\epsilon}=\epsilon_1+i\epsilon_2$, or the complex refractive index, $\tilde{N}=n+ik$, each as a function of photon energy, are poorly known, especially in the (10—30)-eV region and above. A recent compilation[1] of optical data points out that the data for Au are not self-consistent in the Kramers-Kronig sense, in part because they have been measured by a number of techniques and on samples of different types, and the data were then patched together. Even fewer data are available for Ag. In the following we report on measurements of the reflectance of single crystals of Ag and Ag films. The data were obtained with the use of synchrotron radiation and cover the range 3.5—30 eV. The data were Kramers-Kronig analyzed to obtain the dielectric functions and related functions.

An ideal sample for optical studies is flat, strain free and devoid of oxides or other overlayers. No such samples have ever been used and different sets of data differ in the compromises made in samples and in the effect the compromises have on the measurement technique. Thin transparent overlayers have negligible effect on the reflectance of good metals in the visible region, but in the vacuum-ultraviolet (vuv) region most overlayers are absorbing and the errors can be large, up to 10% or so for a monolayer in some cases. Moreover, in the vuv, surface roughness on a submicroscopic scale causes the incident radiation to be scattered nonspecularly, lowering the measured reflectance. Finally, strains can broaden interband structures in the dielectric function, but this may not be a serious problem in the vuv where excited-state lifetime broadening may dominate.

A recent study by Aspnes *et al.*[2] on Au-film samples was directed at explaining the discrepancies in the optical data on Au in the (1—6)-eV region, discrepancies far larger than the individual author's estimated experimental errors. (Aspnes *et al.* cite 28 other studies of the optical properties of Au in this spectral region.) They conclude that in the Drude region (not relevant for our data) the differences arise from different grain sizes in the film samples which alter the scattering parameter in the Drude term. In the interband region the differences arise from surface regions of lower density, essentially grain boundaries, or the open spaces on rough surfaces, both of which were modeled by an effective-medium theory to represent a composite surface region composed of metal and vacuum (air). The effect of the voids was to lower the observed reflectance from that of the metal alone, and to lower the resultant magnitude of the imaginary part of the dielectric function. Other sample problems, strain and surface oxides, seemed to give smaller effects, but the oxides were probably transparent below 6 eV.

Accordingly, we have chosen to use chemically polished Ag single-crystal samples. These are strain free and generally have a minimum of submicroscopic roughness. There is large-scale roughness ("waviness") but the effect of this on the reflected beam is similar to defocusing, and we collect a 6° spread of the reflected radiation. The chemical polishing may deposit a protective layer on the surface. To test the effect of such contamination we examined several crystallographically inequivalent surfaces of single-crystal Ag, and we evaporated films of Ag, *in situ*, on chemically polished single crystals and on glass. The latter was done to separate the effects of surface contamination from roughness-induced scattering at the surface. We were able to demonstrate deleterious effects of surface films on the vacuum-ultraviolet reflectance.

EXPERIMENTAL

The silver single crystals were polished with a series of Al_2O_3 abrasives, then chemically polished by immersion alternately in a 1:1 solution of 50 mol % H_2O_2 and 0.42*M* NaCN in H_2O and in a 0.77*M* aqueous solution of NaCN. The first reagent oxidized the silver, tarnishing it brown, while the second reduced the oxide and gave a bright surface which was then immediately rinsed and dried. These operations were repeated several times to get a surface which appeared smooth and bright and which gave a high reflectance in the (15—25)-eV region. The chemical polishing was carried out in a nitrogen atmosphere and the samples were transported and loaded into the vacuum chamber under the same atmosphere.

The (100) and (111) faces appear to be chemically different; the (100) face yielded a good finish more rapidly. This indicates that the two faces may have had different surface morphologies and different residual overlayers of oxide or cyanide. After reflectance measurements had been made on the Ag single crystals, films of Ag were evaporated on them *in situ* and the reflectance remeasured. The pressure during evaporation was in the 10^{-7}-Torr range. In addition, films were evaporated under the same conditions onto glass substrates.

The vuv reflectances *R* were measured with the use of *p*-polarized synchrotron radiation at 10° incidence with a reflectometer described previously.[3] Several detectors, choppers, and filters were used to reduce second-order and scattered radiation. Nevertheless, the grating used was not optimal and corrections for scattered radiation were made subsequently. The entire (3.5—30)-eV region was covered in intervals of varying size to ensure that no structure in the reflectance was missed.

RESULTS

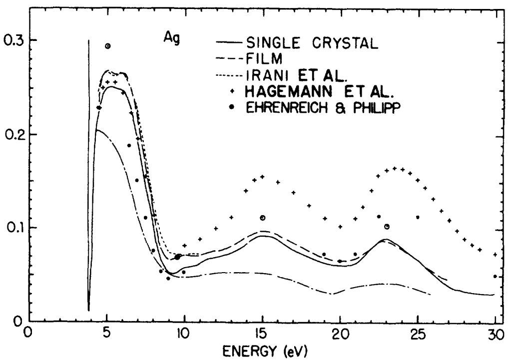

FIG. 1. Reflectance of silver. Solid line—present work on chemically polished single-crystal face, dashed line—present work on film on glass, dotted-dashed line—single crystal, polished, measured before chemical etch, short dashed line—from Irani, Huen, and Wooten (Ref. 9), crosses—from Hagemann, Gudat, and Kunz (Ref. 1), dots—from Ehrenreich and Philipp (Ref. 10), and circles—ideal reflectances from Table I.

The reflectance of a mechanically polished crystal of Ag is shown in Fig. 1 both before and after the chemical polish. The two single-crystal faces, (100) and (111), gave the same spectrum within experimental error. This is expected for cubic crystals only if surface layers and surface roughness are nearly the same on all samples. The reflectance of an *in situ* evaporated film on glass is also shown. The curve of the reflectance of a Ag single crystal after polishing with Al_2O_3, but before chemical polishing, is considerably lower than the other curves, especially in the (5—7)-eV and (13—26)-eV ranges. As the surface of such a polished sample is strongly strained, we see then the effects of strain, which decreases and smoothes the vuv reflectance. On the other hand, since any overlayer is absorbing in the 15-eV range, we can then assert that in this range an ideal surface gives the highest reflectance. (This justifies the method used to test our chemical polishing.)

We now compare our experimental curves in Fig. 1.

(i) The reflectance of an evaporated film on a crystal (not shown in Fig. 1) appears intermediate between those of mechanically polished crystals and chemically polished (strain-free) crystals, suggesting a considerable amount of strain in our films.

(ii) The reflectance of the film evaporated on glass is consistently higher than the reflectance of the film deposited on a "clean" crystal (not shown in Fig. 1), though the films were evaporated under the same conditions. This points out the possibility of some geometrical defects on the crystal surface, leading to the loss of part of the reflected light. This appears to be a long-wavelength roughness, i.e., waviness, leading to a loss of reflected light by specular reflection away from the detector rather than submicroscopic roughness, whose loss by scattering should depend strongly on photon energy.

If we accept these deductions we can estimate the value of the reflectance of an ideal Ag crystal in correcting the measured clean-crystal value by the ratio of reflectance (film on glass)/(film on crystal). These estimated values may represent the maximum value of reflectance achievable on Ag, i.e., strain free and unoxidized, and are reported in Table I. (This does not correct adequately for scattering by submicroscopic roughness.)

The spectra of Fig. 1 have been Kramers-Kronig analyzed to obtain the dielectric functions (Figs. 2 and 3) and the loss function (Fig. 4). Unpublished[4] absorbance, $A=1-R$, data in the (0.16–2.8)-eV range were used for the low-energy extrapolation of our curve. The high-energy extrapolation was computed to 105 eV from absorption data by Haensel *et al.*[5] which fit very well with our data. Above 105 eV we used the compilation of Hagemann *et al.*[1]

A listing of most previous optical data on Ag can be found in Ref. 6. We mention here only those in the region above 6 eV. Multiple-angle reflectance data have been taken on Ag films by Robin,[7] Canfield and Hass,[8] and Irani, Huen, and Wooten,[9] the latter in ultrahigh vacuum (UHV) on films prepared *in situ*. Philipp and Ehrenreich[10] measured reflectance at normal incidence followed by a Kramers-Kronig analysis. In some cases these measurements, made with the use of conventional radiation sources, were limited to discrete wavelengths. Electron-energy-loss data have been taken by Daniel[11] and by Schlüter[12] as well as by Wehenkel and Gauthé.[13] These data usually require a Kramers-Kronig analysis and a fit to one independently determined value of $\tilde{\epsilon}$ to get the magnitude of ϵ_1 and ϵ_2 correctly. Thus it is not surprising that all these results are widely spread.

In comparing our data with those of others it is best to compare our measured reflectance spectra with those measured by others. However, in some cases the reflectance was not measured, but was derived from other measurements. Our derived spectra, those of $\tilde{\epsilon}$, can be compared with $\tilde{\epsilon}$ spectra of others, albeit sometimes derived from measurements of different quantities. In so doing, it is entirely possible to find rather good agreement between two data sets in one spectrum, e.g., that of ϵ_1, and poorer agreement in others, e.g., ϵ_2 and R, so a careful check of consistency is needed. Let us now examine the literature data and compare with ours.

The general magnitude of the reflectance above 10 eV is in good agreement with the measured spectrum of Ehrenreich and Philipp[10] (on an electropolished polycrystal) except at the end of their experimental range, near 22 eV, where the earlier reflectance spectrum rises rapidly. Our 11.5-eV structure is missing and the reflectances between 5 and 8 eV seem too low. The same comments can be made in comparing the ϵ_2 spectra, except that there is rather good agreement in magnitude in the (5–8)-eV region as well. The ϵ_1 values of Philipp are consistently higher than ours and do not go negative between 5 and 7 eV. The discrepancies in ϵ_1 could arise both from the use of different reflectance data and from different extrapolations in the Kramers-Kronig analysis. The magnitude of the reflectance spectrum of Robin[7] (not shown in the figures) is consistently lower than ours in all ranges, but particularly in the (4–10)-eV range; moreover, the energies of their structures differ notably from ours. These results, obtained with strained films, are typical of early low-resolution measurements.

Irani, Huen, and Wooten[9] measured the reflectance at a number of angles of incidence and fit the dielectric function to the data. We compare their dielectric function and the reflectance calculated from it with our data. Their data extend up to 11 eV. The reflectance of their thin-film samples is in excellent agreement with our film reflectance and is consequently a bit higher than our single-crystal reflectance. There is similarly good agreement in ϵ_1 and ϵ_2 with the structure at 10 eV comparably well resolved in ϵ_1.

We also emphasize that some authors report ϵ_2 values at the 4.5-eV maximum slightly higher (up to 4.1) than ours (3.77). These values, measured with films on quartz, by Huebner *et al.*[14] and by Meyer

TABLE I. Reflectances of Ag.

Sample	Energy (eV) 5	9.5	15	23
Clean crystal	0.250	0.053	0.092	0.089
Film on crystal	0.228	0.053	0.080	0.074
Film on glass	0.268	0.068	0.098	0.088
Estimated ideal value (see text)	0.294	0.068	0.113	0.106

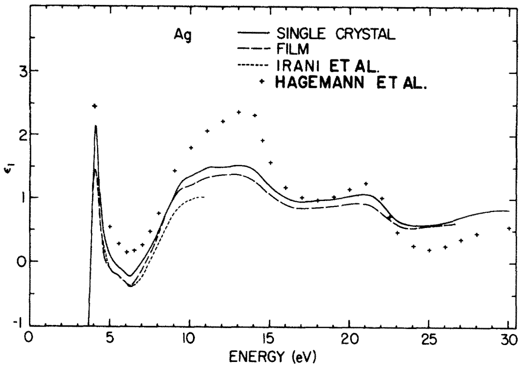

FIG. 2. Real part of the dielectric function of Ag derived by Kramers-Kronig analysis of the reflectance of Fig. 1. Solid line from single-crystal data and dashed line from film data. Short dashes—from Ref. 9 and crosses—from Ref. 1.

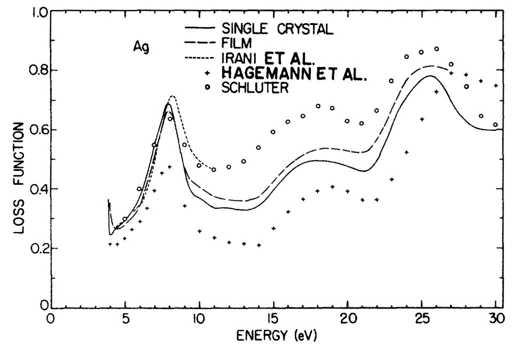

FIG. 4. Electron-energy-loss function $\mathrm{Im}(-1/\tilde{\epsilon})$ for Ag from the dielectric function of Figs. 5 and 6 (solid line). Open circles—energy-loss function $\mathrm{Im}(-1/\tilde{\epsilon})$ for Ag from Schlüter (Ref. 12).

et al.,[15] for instance, are compatible with our estimated "ideal" reflectance value at 5 eV in Fig. 1.

It seems then that high reflectance (or high ϵ_2) in the 4.5-eV region can be used to check the quality of the surface: low strain, low roughness; these features also give a steep rise at 3.9 eV in ϵ_2 as pointed out by Wisemius *et al.*[16] but care should be taken with the use of such a test alone because some authors also report high R and ϵ_2 at 5 eV on strongly disordered or amorphous Ag films (Canfield and Hass[8] and Rivory and Théye[17]).

From 1.8 to 3.8 eV our ϵ_2 curve, calculated from Weaver's $(1-R)$ data,[4] is lower and flatter than most of the literature values. This difference is due, in part, to the low temperature at which these data were taken. This part of the spectrum is comparable only with the careful measurements of Johnson and Christy[18] on thin films deposited on quartz. This points out the possibility that low-ϵ_2 (or n) values in the visible range are also a test of quality of the Ag surface. In any case, a check of the reflectance at 15 or 23 eV seems to be needed.

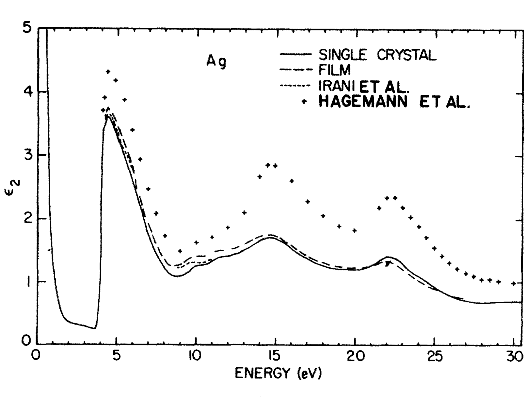

FIG. 3. Imaginary part of the dielectric function of Ag derived by Kramers-Kronig analysis of the reflectance of Fig. 1. Solid line—from single-crystal data and dashed line—from film data. Short dashes—from Ref. 9 and crosses—from Ref. 1.

Energy-loss spectra and absorption of thin films are naturally less affected by defects on surfaces. Let us compare our results with such data.

The comparison between the energy-loss spectrum $[-\mathrm{Im}(1/\tilde{\epsilon})]$ measured on thin unsupported films by Daniels[11] or by Schlüter[12] is in good agreement with our calculated $-\mathrm{Im}(1/\tilde{\epsilon})$ curve (Fig. 4), particularly in the overall shape of the spectrum. The magnitude of our calculated spectrum is lower than the measured ones in the (10—25)-eV range; this can be correlated with our probably low experimental R and calculated ϵ_2 values. The 10- and 11.5-eV structures are not really resolved in the experimental curves.

Finally, the most recent vuv data on silver appears in a recent compilation by Hagemann *et al.*[1] They are the result of absorption measurements on thin films and Kramers-Kronig analysis, with the use of, among others, data from Refs. 8—10. As can be seen, agreement is not very good above 10 eV in any of the figures. Below 11 eV agreement is better as Hagemann *et al.* used the data of Irani *et al.*[9] in their calculation.

All the discrepancies observed between our data and the compilation seem to come from too high an experimental absorption coefficient in the (16—110)-eV range. Some previous absorption data by Haensel *et al.*[6] seem more consistent with our data and all data available in this high-energy range.

In summary we report here a new reflectance curve with better magnitude and resolution than the previous ones. In the vuv range we observe a new small structure at 11.5 eV and refine the positions and shapes of previously observed structures at 15.2, 22.9, and 25.5 eV. The magnitude of the reflectance on an ideal Ag surface in the (10—25)-eV range appears to be no more than 10—15% higher than our experimental data; this point rules out the values given in the recent compilation by Hagemann *et al.*[1] in this energy range.

DISCUSSION

We first comment on the magnitudes of the data. Our data on chemically etched single crystals show that all three faces measured gave the same spectra within experimental errors, about 5% of the measured values. This indicates that the microscopic morphology of the three surfaces is essentially the same for our purposes and that the protective layer left by the polish is of similar composition and depth despite different times necessary to get comparable visual appearances when chemically polishing. These surfaces should have little microscopic roughness and some large-scale waviness which should play some role in the measurements, as some of the off-specular radiation was lost. The overlayer presumably is absorbing and lowers the reflectance somewhat. Measurements on the films evaporated on glass showed somewhat higher reflectances yet well-resolved structures. Although our vacuum was no better than 10^{-7} Torr, our film data are in excellent agreement with those of Irani, Huen, and Wooten,[9] except at the high-energy limit of their spectral range. Thus we feel the best experimental spectra, i.e., those most representative of Ag, are probably our "film" data. These are what were Kramers-Kronig analyzed and presented. The "true" reflectance of strain-free atomically clean Ag is higher, as indicated by a few points in Fig. 1, but not more than 15% higher. This will lead to higher values of ϵ_2.

Recently Lässer, Smith, and Benbow[19] calculated the dielectric functions of Cu, Ag, and Au with the use of an interpolation scheme for the band structure. They evaluated the electric dipole matrix elements from the derivatives of the energy eigenvalues with respect to wave vector. Figure 5 compares our ϵ_2 spectrum with their calculated spectrum and with the spectrum they originally used for comparison.[1] It is clear that our spectrum is considerably closer to the calculated spectrum throughout the entire vuv region. Corrections for surface oxide and strain could raise our ϵ_2 spectrum, but not more than 15% at any energy.

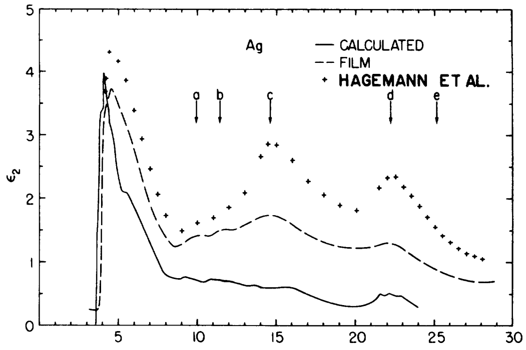

FIG. 5. Imaginary part of the dielectric function for Ag. Solid line—calculated (from Ref. 19), dashed line—present work (film), and crosses—from Ref. 1. Letters label transitions discussed in the text (see Table II).

Moreover, we find in general that ϵ_2 above 10 eV for Ag is lower than that for Au, a feature also found in the calculated spectra but not in all previous data. There are many small structures in the calculated spectrum not evident in the experimental spectrum, but these may easily be rendered undetectable by thermal broadening, lifetime broadening, or small shifts in energy or oscillator strength. The largest discrepancy, besides the fact that the calculated magnitude of ϵ_2 for Ag is about a factor of 2 too small, is the lack of the 14.5-eV peak which appears only as a plateau in the calculated spectra.

Examining the contribution of individual band pairs in the ϵ_2 calculation reveals some possible correlations noted in Table II. The corresponding calculated matrix elements seem to be too low to match the magnitude of the experimental structures.

The spectra of Ag in the vuv range were taken with a sufficient number of data points and with

TABLE II. Optical structures in the (8—30)-eV range for Ag (energy of structures given in electron volts).

Labels in Fig. 5	R	ϵ_2	$-d^2\mu/dE^2$	$\Delta T/T$ (Ref. 21)	Individual band contributions (Ref. 19)
		(Our results)			
a	10.0	9.9	10.0		3,4,5→7
b	11.4	11.4	11.3		5,6→8
c	15.2	14.6	15.2	15.6	4,5→9 and 1,2,3→8
d	22.9	22.2	22.6	22.6	2,3→8,9 and 3,4,5→10
e	25.0		25.1	25.3	1,2,3→10

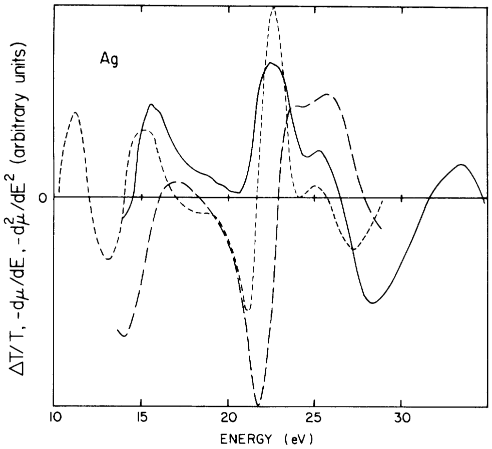

FIG. 6. Derivative transmission spectra for Ag. Solid line—thermotransmission spectrum (essentially the negative of the temperature derivative of the absorption coefficient μ) from Ref. 21. Dashed line: $-d\mu/dE$ from present data. Dotted line: $-d^2\mu/dE^2$.

good enough statistics to allow differentiation of the spectra. We calculated the energy derivatives of the absorption coefficient μ for comparison with thermotransmission spectra[20,21] as the relative change in transmission is directly proportional to the negative of the change in absorption coefficient. For Ag (Fig. 6) the thermotransmission[21] is simple and rather closer in shape to the $-d^2\mu/dE^2$ than to the first derivative, indicating that broadening is largely responsible for the thermotransmission spectrum.

It should be remarked that exact agreement of energy derivative and thermotransmission spectra is not expected because different spectral features, although possibly all resembling the second derivative of the absorption coefficient, will have different amplitudes, thus appearing with different weights in the thermotransmission spectrum.

ACKNOWLEDGMENTS

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