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Optical reflectance of liquid mercury

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Normal-incidence and grazing-incidence reflectances of liquid Hg have been measured in the visible region at room temperature (24 °C). The results were consistent with the optical properties determined by ellipsometry. No evidence was found for transition layers on the surface of liquid Hg.

The optical response of liquid Hg has long been considered to be anomalous.[1] Some of the reflectances measured in the near infrared to the near ultraviolet do not agree with those calculated from the optical constants determined by ellipsometry. The former have yielded good agreement with those given by the classical Drude formula, whereas the latter consistently show slight differences from the Drude values. As will be shown below, in the case of the normal-incidence reflectance measured under vacuum,[2] the discrepancy amounts to roughly 0.012 in the absolute reflectance value in the photon energy region from 1.24 to 2.75 eV. For the last two decades, this puzzling result has been considered by some to result from an intrinsic interfacial structure in liquid Hg. Models of the surface transition layer, across which the values of the optical constants vary continuously from the bulk values of liquid Hg to those of the ambient medium have been proposed[1] to reconcile the apparently conflicting experimental results.

Several years ago, we critically reviewed the experimental results of the optical measurements on liquid Hg.[3] We found that the ellipsometric data, taken under various ambient media and at several angles of incidence, are internally consistent within the regime of Fresnel optics. Furthermore, our reflectance measurements for a quartz–liquid-Hg interface at an angle of incidence $\theta = 60.5°$ were found consistent with ellipsometric measurements on the same surface. It was also pointed out that similar consistency was found for a previous experimental result[4] obtained for a quartz–liquid-Hg interface at $\theta = 70°$.

This problem has been revisited recently by Schaich[5] who analyzed the apparent conflict between the reflectance and ellipsometric measurements in terms of the d-parameter formalism, which added interfacial effects to Fresnel optics. He concluded that a careful remeasurement of the reflectances at both normal and oblique angles of incidence was necessary in order to resolve the problem. Here we report the results of such measurements.

Reflectance measurements of liquid Hg made since 1957 (Refs. 1–4 and 6–9) are summarized in Table I, where the type of reflectance, angle of incidence θ, ambient medium, energy range, year, and name of investigator are tabulated. D (Drude) or ND (non-Drude) in the fifth column denotes agreement or disagreement, respectively, with the Drude values. The earlier data of Schulz[6] and Mueller,[8] which were obtained at either normal incidence or at $\theta = 45°$, agreed with the Drude values while more recent results of Crozier and Murphy[4] and of Inagaki, Arakawa, and Williams,[3] which were obtained

TABLE I. Reflectance measurements on liquid Hg. $\bar{R} = (R_p + R_s)/2$ where R_p and R_s are the reflectances for p- and s-polarized light, respectively. R_N is the normal-incidence reflectance.

Reflectance	θ	Ambient material	E (eV)	D or ND	Investigators	Ref.
$\bar{R}$	45°	Quartz	0.459–5.39	D	Schulz (1957)	6
		Glass	0.729–3.10	D		
		NaCl	0.095–1.24	D		
R_N	~0°	Vacuum	2–19.5	D ($E < 3.5$ eV)	Wilson-Rice (1966)	7
R_N	~0°	Vacuum; He	1.24–2.76	D	Boiani-Rice (1969)	2
R_N	~0°	NaCl	0.413–0.827	D	Bloch-Rice (1969)	1
		CsBr	0.062–0.413	D		
		LiF	0.365–2.50	D		
		KRS-5	0.0413–0.827	D		
R_N	~0°	Al_2O_3	0.5–4.8	D ($E < 3.8$ eV)	Mueller (1969)	8
R_s	45°	Al_2O_3	0.5–4.8	D ($E < 3.8$ eV)		
R_N	~0°	MgF_2	0.5–8.25	D ($E < 3.8$ eV)	Choyke *et al.* (1971)	9
R_p	70°	Quartz	1.71–4.13	ND	Crozier-Murphy (1972)	4
R_s	70°	Quartz	1.71–4.13	ND		
R_p	60.5°	Quartz	0.5–3.7	ND	Inagaki *et al.* (1981)	3
R_s	60.5°	Quartz	0.5–3.7	ND		

at $\theta=70°$ and $\theta=60.5°$, respectively, gave non-Drude values. Therefore, we first remeasured the normal-incidence reflectance of the vacuum-Hg interface which had been measured by Wilson and Rice[7] and by Boiani and Rice.[2] In addition, we measured the normal-incidence reflectance for a quartz–liquid-Hg interface. Since the reflectances R_p and R_s at $\theta=60.5°$ and $\theta=70°$ measured previously[3,4] were for a quartz–liquid-Hg interface, we also measured the reflectances for both polarization states for the vacuum-Hg interface at $\theta=70°$.

The goal of the present experiments was to provide a convincing answer to the question as to whether the measured reflectances are in real conflict with the ellipsometric data. We therefore confined our measurements to the spectral range from 1.65 to 3.10 eV where the discrepancy between the two data sets is most significant. At 2 eV, for example, the reflectance value previously measured[2] for the vacuum–liquid-Hg interface and the one calculated from the ellipsometric data are 0.768 and 0.782, respectively; the discrepancy being only 0.014 in absolute reflectance. Great care was taken in attaining light source stability and detector linearity, in preparing a fresh, contamination-free Hg surface, and in setting up a precise optical alignment in a reproducible manner.

Two separate experiments of the normal-incidence reflectance of free-surface Hg were performed. In the first, reflectance from an air-Hg interface was measured using light from a He-Ne laser at a photon energy of 1.96 eV ($\lambda=632.8$ nm) and from an Ar^+ ion laser operating at 2.41 eV ($\lambda=514.5$ nm) and at 2.73 eV ($\lambda=454.5$ nm). In the second, reflectance from the vacuum-Hg interface was measured using a Xe lamp in the region from 1.65 to 3.10 eV (650–400 nm). The former measurement was made on a large air-supported table while the latter was made under vacuum using a Seya-Namioka monochromator. In both experiments, intensities of the incident and reflected light were measured by a single detector, a Si photodiode and a Hamamatsu R928 photomultiplier, respectively, with an appropriate light diffuser[10] mounted in front of the detector window. The light diffuser was found essential to minimize positional variation of the detector sensitivity. The vacuum-Hg arrangement was similar to that of Boiani and Rice except that our monochromator was placed horizontally and an aluminized mirror was used to direct the incident light down onto the liquid-Hg surface. The angles of incidence used were $\theta=3°$ for the measurements made with the lasers and $\theta=9.5°$ for those made with the Xe lamp. In both experiments, the picoammeters used (Keithley 485) were interfaced directly to a microcomputer. In the vacuum-Hg experiments, the sample surface was refreshed by overflowing liquid Hg (less than 5-ppm impurities) from the bottom of an external reservoir into a plastic cylindrical sample holder. In the air-Hg experiment, the surface was cleaned by repeatedly rolling a fresh piece of transparent adhesive tape on the Hg surface as described by Hayes.[11]

The normal-incidence reflectances measured under air and vacuum are presented in Fig. 1. The values obtained are in remarkably good accordance with those derived from the ellipsometric data.[3] No indication of invalidity of Fresnel optics is evident in these results. Previous measurements made by Boiani and Rice are also plotted in Fig. 1 together with the Drude values. Their values are systematically smaller than the ellipsometric values by roughly 0.012 and, at first glance, appear to be in good agreement with the Drude values. However, their overall photon energy dependence is more similar to the ellipsometric values than to the Drude values.

Measurements of the normal-incidence reflectance for a quartz–liquid-Hg interface were made by overlaying a $\frac{1}{16}$-in.-thick quartz plate on a fresh surface of liquid Hg. The reflectance values for the quartz–liquid-Hg interface were obtained from the results measured for this

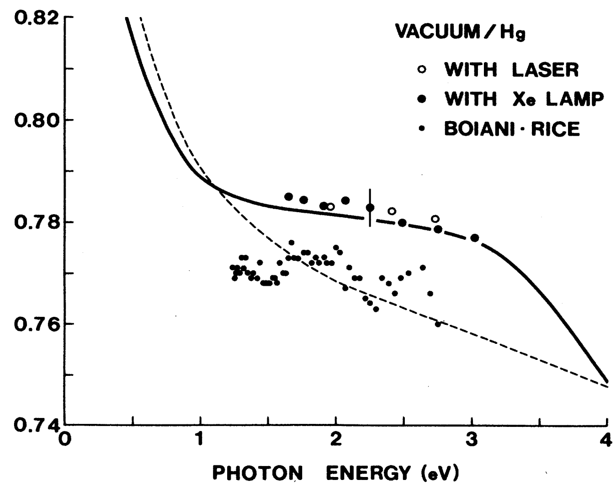

FIG. 1. Normal-incidence reflectance for the vacuum (air)–liquid-Hg interface. Solid and dashed lines represent the reflectances calculated from the ellipsometric data (Ref. 3) and from the Drude formula, respectively.

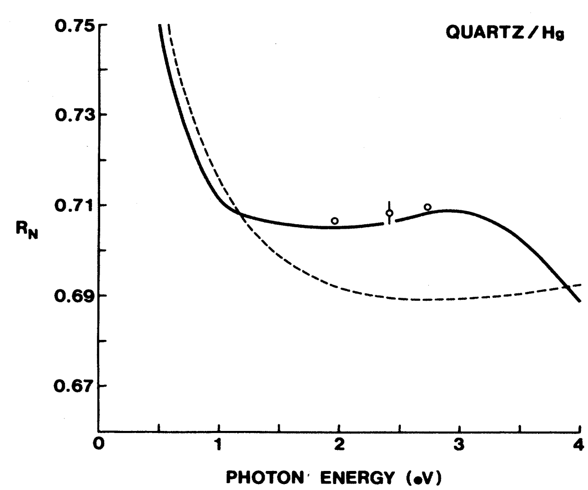

FIG. 2. Normal-incidence reflectance of a quartz–liquid-Hg interface. Solid and dashed lines represent the reflectances calculated from the ellipsometric data (Ref. 3) and from the Drude formula, respectively.

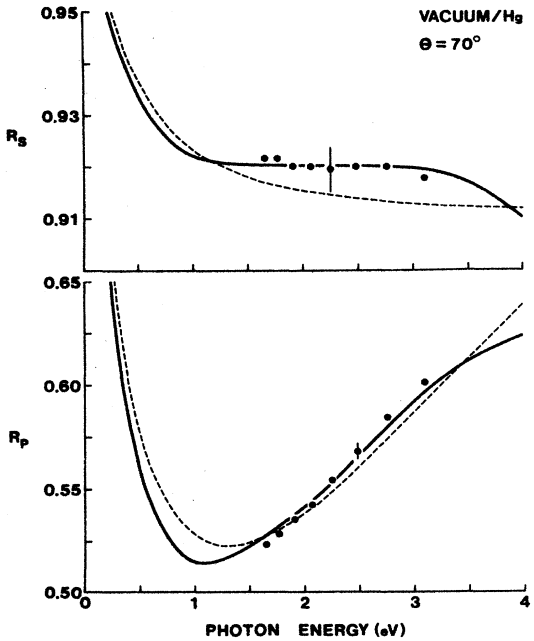

FIG. 3. Reflectances for s- and p-polarized light at $\theta = 70°$ for the vacuum–liquid-Hg interface. Solid and dashed lines represent the reflectances calculated from the ellipsometric data (Ref. 3) and from the Drude formula, respectively.

air–quartz–liquid-Hg system after correcting for the effect of multiple reflections in the quartz plate by the method described by Bloch and Rice.[1] Presented in Fig. 2 are the results with the lasers at three different photon energies. They also exhibit good agreement with the ellipsometric values and are distinctively different from the Drude values. These data are in contrast to those reported previously by Bloch and Rice[1] and by Mueller[8] who obtained Drude values for Hg in contact with LiF and sapphire, respectively, in this spectral region (see Table I).

The reflectances measured under vacuum using s- and p-polarized light at $\theta = 70°$ are presented in Fig. 3. In this case, the differences in the Drude and ellipsometric reflectance values are considerably smaller than in the case of normal incidence and amount to less than 0.008 for both photon polarizations. Nevertheless, it is clear from Fig. 3 that the results are consistent with the ellipsometric values and clearly deviate from the Drude values.

In summary, we have confirmed, with sufficient experimental precision, that the reflectances measured at both normal and grazing incidences deviate clearly from the Drude values and are in good agreement with the results from ellipsometric measurements. The present results provide no evidence for transition layers on the surface of liquid Hg.

Finally, we note that attenuated-total-reflection (ATR) measurements have been made on liquid Hg in the Otto geometry by several authors in which photon-to-surface-plasmon conversion has been observed.[12–14] It was reported that the results of the ATR measurements deviate from those of ellipsometric data. This has been taken to be additional experimental evidence for the transition-layer hypothesis. Now that the reflectance data have been found not to be contradictory with the ellipsometric data, it may be necessary to reinterpret the ATR data.

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