STUDY OF PHYSICS AND CHEMISTRY OF SURFACES FROM FRUSTRATED TOTAL INTERNAL REFLECTIONS

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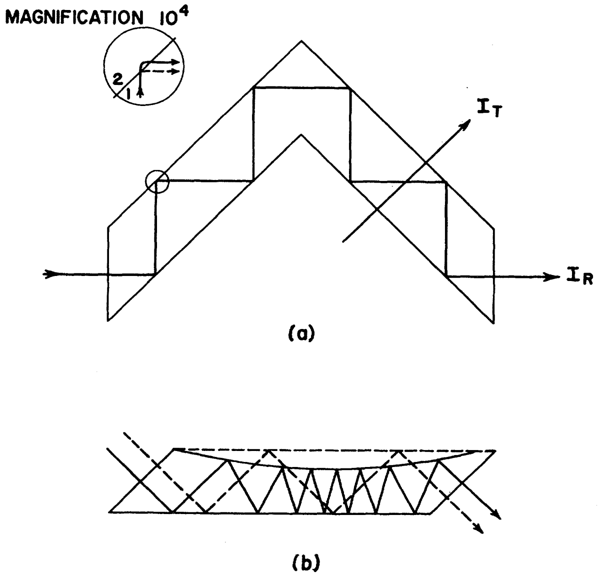
It has been suggested[1] that the physics and chemistry of surfaces of optically transparent materials, particularly semiconductors, may be studied through the analysis of the spectrum of totally internally reflected radiation. This seems feasible since it is known that the totally reflected radiation actually penetrates the surface into the rarer medium to a depth given by

$$x_{1/2} = \frac{0.693\,\lambda_1}{2\pi(\sin^2\theta - n_{21}{}^2)^{1/2}}.$$

Here λ_1 is the radiation wavelength in the denser material, θ the angle of incidence, and n_{21}, which is less than unity, is the relative index of refraction.[2] The penetration depth is about one-tenth of a wavelength except near the critical angle; where $\sin\theta \simeq n_{21}$, the penetration depth becomes large. Goos and Hänchen[3] demonstrated this effect in a remarkable experiment where they actually measured a displacement, proportional to the penetration depth, of the internally reflected beam compared to metallic reflection as shown in the insert of Fig. 1(a).

It is the purpose of this note to give experimental evidence indicating that infrared radiation which penetrates the surface interacts with impurities on the surface at molecular resonance frequencies and that this interaction is comparable to what would be observed in a transmission measurement for impurity films on the surface thinner than a penetration depth. Since there is a prohibitive power loss in transmission through several separated layers whereas internal reflections are total, the reflection technique has the obvious advantage over transmission measurements where many encounters with the surface are necessary in order to gain sensitivity.



(a)

(b)

FIG. 1. Sample shapes for total internal reflection measurements.

The sample[4] used is shown schematically in Fig. 1(a) where the angle of incidence is 45 degrees. It was cut, ground, and diamond-polished in one piece from 30 ohm-cm, p-type germanium. The entrance face had dimensions of about 1/4 in. ×3/4 in. It should be noted that after eight reflections the exit beam is axial with the entrance beam, which simplifies the optics of the infrared spectrometer. With narrow spectrometer slits, thin samples can be used and the number of reflections can thereby be increased for the same length of sample. Figure 1(b) shows how the number of reflections can be increased by curving the surface in an appropriate way. On each reflection the angle of incidence is increased. Care has to be taken so that the angle of incidence is not decreased beyond the critical angle when the beams would be lost. To see if this technique might work, known impurities were placed on the surface and their spectra were analyzed with the aid of a Perkin-Elmer Model 12C spectrometer.

The sample shown in Fig. 1(a) was mounted in a cell so that all of the surfaces except the entrance and exit faces could be exposed to a liquid or a gas. Figure 2 compares the spectrum of the sample with no impurities intentionally added to the surface to that observed when water surrounded the sample. The 3- and 6-micron water absorption bands are clearly visible in the latter case. When the signal strength of the 3-micron band was compared to that observed in a transmission measurement through a thin film of water, the depth of penetration was determined to be about 0.15 micron, assuming a comparable strength of interaction in the transmission and

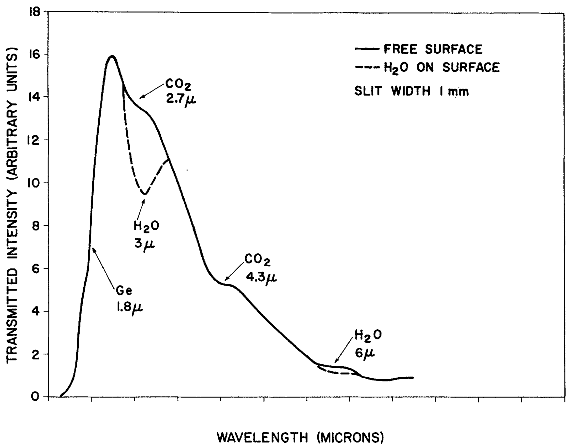


FIG. 2. Spectra of beam I_R of Fig. 1(a). The lines attributed to CO_2 indicate its presence in the atmosphere.

reflection measurements. This depth of penetration compares favorably with that calculated from theory.

A series of measurements was next made on the 3.4-micron polyethylene line. The polyethylene was dissolved in xylene to a dilution of 0.04 % by weight and sprayed on the surface of the sample. The signal from transmission and reflection could be directly compared by analyzing the spectra from I_T and I_R in Fig. 1(a). The results of these measurements are shown in Fig. 3. The signal in the reflection beam does not increase with film thickness beyond a certain film thickness. The transmission signal, however, increases with thickness. For a film thickness of less than about 0.5 micron, the signal from eight reflections is greater than that from two transmissions. When we compare two reflections to two transmissions we see that the signal strengths are comparable for a film thickness less than about 0.16 micron which is also the thickness beyond which the signal strength in the reflection measurements does not increase. This is thus a measure of the penetration depth of the radiation in the rarer medium. Figure 4 shows the penetration depth of the polyethylene-germanium system, whose indices of refraction are 1.5 and 4, respectively, as a function of angle of incidence as computed from the formula in the first paragraph. We see that depth determined experimentally falls right on the theoretical curve.

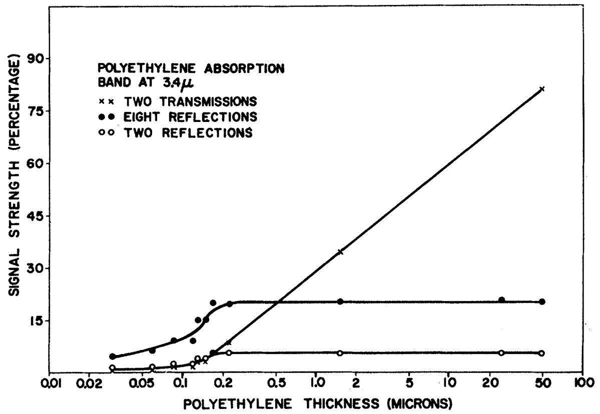


FIG. 3. Comparison of the signal strength for transmission and reflection beams, I_T and I_R of Fig. 1(a), for the polyethylene absorption line at 3.4 microns. The spectrometer slit width was 0.5 mm for these measurements.

These results indicate that the radiation which penetrates into the rarer medium does interact with the surface impurities at molecular resonance and that the interaction strength is comparable to that occurring in transmission meas-

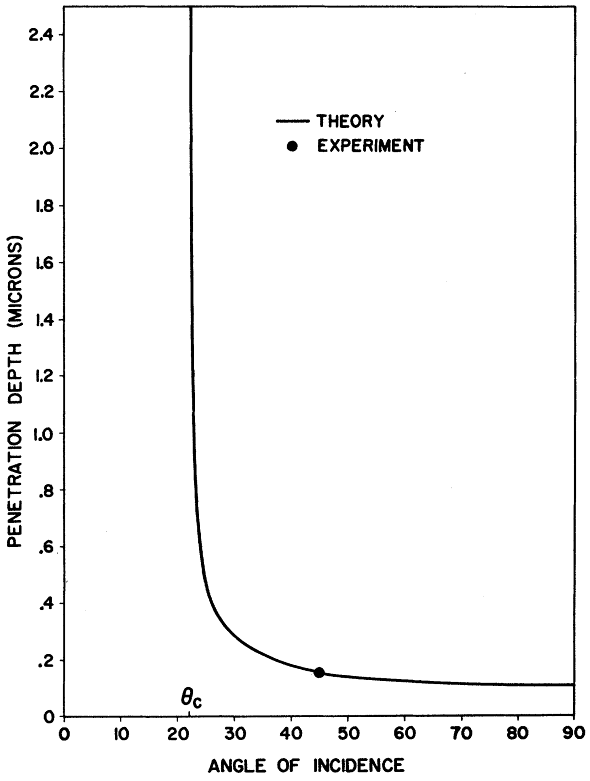


FIG. 4. The penetration depth versus angle of incidence for total internal reflection at the germanium-polyethylene interface. The experimental point is obtained from the experimental data of Fig. 3.

urements for films whose thicknesses are equal to or less than the penetration depth. Furthermore, this interaction does not represent just a power loss at resonance resulting from an increase in the refractive index in the polyethylene, and thus upsetting the condition of total internal reflection at the germanium-polyethylene interface. If this were the case, the reflected radiation would always penetrate the whole of the polyethylene film and any radiation not absorbed would be reflected from the polyethylene-air interface and the signal strength would always increase with film thickness. Near the critical angle such an effect could undoubtedly be observed.

Our results indicate that through the use of a more sensitive spectrometer and more reflections this technique should indeed work in the study of surface chemistry and we expect that it should be possible to detect one to ten atomic layers. Furthermore, such a technique should be valuable in the study of thin films.

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[1] Discussion by N. J. Harrick following paper by R. P. Eischens at Second Conference on Semiconductor Surfaces, Naval Ordnance Laboratories, White Oak, Maryland, December, 1959 [J. Phys. Chem. Solids (to be published).] It was brought to the author's attention after the work described here was completed that Dr. J. Fahrenfort of the Royal Dutch Shell Laboratories, Amsterdam, has described what appears to be a similar technique to observe the spectra of organic materials on silver chloride at the Fourth International Congress on Molecular Spectroscopy, Bologna, September, 1959 (unpublished).

[2] Julius A. Stratton, Electromagnetic Theory (McGraw-Hill Book Company, Inc., New York, 1941).

[3] F. Goos and H. Hänchen, Ann. Phys. 1, 333 (1947).

[4] Semiconductor samples similar to these have been used in the study of other properties of semiconductor surfaces. N. J. Harrick, J. Phys. Chem. Solids 8, 106 (1959). N. J. Harrick, J. Opt. Soc. Am. 49, 376 (1959).

MECHANISM OF ANTIFERROMAGNETISM IN CHROMIUM

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An experiment is proposed which may in principle distinguish between three mechanisms of antiferromagnetism, one of which may obtain in chromium. Corliss, Hastings, and Weiss[1] have observed that each magnetic superstructure reflection in the neutron diffraction of a Cr single crystal is split into six spots equidistant from the reciprocal lattice point and which lie along [100] type directions from that point. This result can be interpreted in several ways:

A. Cr has basically a Néel type antiferromagnetic structure, but with periodic antiphase domains.[1]

B. The localized spins lie in a (100) plane and spiral with a fixed period in the direction perpendicular to the plane.[2]

C. The localized spins are oriented by their interaction with a static spin density wave in the conduction electron gas.[3]

Each antiferromagnetic domain (or group of antiphase domains for case A) contributes to two of the six magnetic reflection spots associated with a given reciprocal lattice point. That all six spots occur [and, for example, have equal intensity at the (1, 1, 1) point] indicates that the unit vector $\vec{\lambda}$ characteristic of a given domain (as defined below) is parallel or antiparallel to one or the other of the three [100] type axes on a statistically equal basis. For the three models under consideration, $\vec{\lambda}$ is:

A. perpendicular to the antiphase domain boundaries;

B. parallel to the axis of the spiral;

C. parallel to the wave vector of the spin density wave.

An experiment of potentially great interest it to cool a single crystal of Cr through the Néel point to low temperature in a large magnetic field parallel to a [100] crystal axis, and then to study the relative intensities of the six magnetic reflection spots. If the applied field is sufficient to upset the statistical equality of the three [100] axes with regard to $\vec{\lambda}$, the relative intensities of the spots will be modified, and should allow one to distinguish between mechanisms A, B, and C, or at least between C and A or B. Such field-cooling effects may reasonably be anticipated.

Magnetic dipole-dipole interactions contribute