CHEMISTRY LETTERS, pp. 1077-1080, 1983.

THE MEASUREMENT OF INFRARED REFLECTION-ABSORPTION SPECTRA OF THIN POLYVINYLACETATE FILMS FORMED ON SILICON SURFACES

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Infrared reflection-absorption spectra of thin polyvinylacetate films formed on silicon surfaces have been measured by both double-beam and polarization modulation methods. The spectrum is observed as a reflectivity maximum or minimum depending upon the angle of incidence. It is shown that polarization modulation method is extremely useful for investigating surface films on silicon.

Among a variety of surface-vibrational spectroscopies, infrared reflection-absorption spectroscopy (IRRAS) has provided a high-sensitive means of obtaining vibrational spectra of adsorbed molecules or thin films on specularly reflecting metal surfaces. Recently a considerable progress has been achieved in IRRAS by incorporating modulation methods^1) which contribute significantly to the improvement of a signal-to-noise ratio, thereby permitting detection of faint signal more easily than ever.

In the last few years, a growing need has been placed, particularly in the field of semiconductor technology, on the elucidation of the full structure of surface contaminants such as naturally adsorbed species which influence seriously on device performance. Although until now it is not yet definitely known that polarization-modulation IRRAS can be applied to semiconductor surfaces, it is of considerable interest to explore this possibility. Actually, Allara et al.^2) have previously measured the infrared spectrum of a polymethacrylate film prepared on a silicon mirror by means of a conventional IRRAS and have investigated theoretical fitting of the band shape observed. Nevertheless no other data showing the utility of IRRAS has been presented in the literature.^2) From this point of view, we attempted for the first time to apply a polarization-modulation IRRAS technique to the measurement of surface films at Si/air interface. The present report summarizes the results obtained for thin films of polyvinylacetate (PVAc) on silicon substrates.

Films of PVAc were prepared by dropping acetone solution of known concentration onto polycrystalline Si surfaces, optically polished with alumina on a buff. The thicknesses of the films were estimated from the measured amounts of the solution, assuming a density of 1.2 $g \cdot cm^{-3}$ for PVAc.

Conventional reflection-absorption spectra were measured with a JASCO A302 grating spectrophotometer equipped with an SRS-1 reflection accessory operative at wide range of angles of incidence. Measurements were also performed with a JASCO polarization-modulation IRRAS spectrophotometer. The details of the instrument will be described elsewhere.^3) In brief, radiation emitted from the source is divided by mirrors into two beams, which are then passed through fixed polarizers producing p- and s-polarized radiation respectively. A rotating sector mirror makes alternate pulses of 140 Hz incident on the sample at an angle of incidence of 80°. The reflected beams are dispersed by a grating of the monochromator and are filtered, and then focussed on a liquid-nitrogen cooled InSb/HgCdTe dual detector. In order to remove the undesirable polarization dependence characteristic of the grating, the monochromator was oriented at 45°

with respect to the polarization planes of the incident beams. The alternating signal at the detector is preamplified and sent to a Brookdeal 9503 Lock-in amplifier. The imbalance of the intensity of the p- and s-polarized radiation in the whole optical system is compensated by using an attenuator placed in the s-polarized beam.

In IRRAS, a maximum sensitivity for reflection-absorption can be obtained with p-polarized radiation incident on a highly conducting metal surface at near glancing angle at which maximum strengths of standing electric fields are produced by the superposition of the incident and reflected waves as a result of the phase change on reflection. This property stems from the value of the complex refractive index, $\hat{n} = n - ik$, where $k \gg n$ for metals in the infrared. On the other hand, the use of IRRAS for measuring surface films on semiconducting materials suffers from the problem associated with an unavoidable decrease in reflectivity due to $k \ll n$. For silicon, k is zero hence the reflectivity of p-polarized radiation decreases to a minimum of zero at the angle of incidence θ_B defined by Brewster's formula, $\theta_B = \tan^{-1} n$. Accordingly one would expect the optimum angle of incidence for Si to be either larger or smaller than θ_B. To examine the best of the angle of incidence experimentally, p-polarized spectra of a PVAc film 80 nm thick on Si were measured as a function of the angle of incidence using a conventional double-beam technique. To remove the interference of absorption due to atmospheric water and also to improve the S/N ratio, 16 numbers of scans of a background and a sample spectrum were averaged digitally, followed by subtraction.

Figure 1 shows the results obtained for the carbonyl stretching vibration band. The spectra change in intensity and shape depending upon the angle of incidence; the reflectivity change due to the absorbing film is either positive or negative depending upon whether $\theta > \theta_B$ or $\theta < \theta_B$. These observations are well accounted for by the following calculations based on the simple model proposed by McIntyre and Aspnes.[4)] They have derived approximate expressions of normalized reflectivity changes, $\delta R/R$, for p- and s-polarized radiation due to the introduction of an absorbing surface film sufficiently thin compared to the wavelength: δR ($= R' - R$) represents the reflectivity change where R' and R are the reflectivities of the substrate with and without the film, respectively. This model well meets the present investigation, and we calculated $\delta R/R$ versus angle of incidence for both polarizations. However, since δR is a useful quantity which determines the magnitude of absorption intensity to be observed, $\delta R/R$ was converted into δR multiplying by R computed with Fresnel's reflection coefficients. In these calculations, values of $n = 3.42$ and $k = 0$ for Si were used while for PVAc $n = 1.4$ and $k = 0.5$ were assumed tentatively. Figure 2 illustrates the results.

It can be seen in Fig. 2 that for s-polarized radiation δR remains nearly constant for $\theta = 0^\circ$ up to 40° and gradually decreases with increasing angle of incidence. The sign of δR is always positive. In contrast, the variation of δR for p-polarized radiation is more complicated; there are two particular angles at which δR changes its sign: one is the Brewster angle where R falls to zero and therefore δR must be zero; the other is the angle where δR becomes zero by itself. For angles greater than θ_B, δR at first increases steeply then reaches a maximum at 86° and finally becomes zero at grazing incidence. This behavior of δR for p-polarized radiation is in harmony with the experimental observations shown in Fig. 1.

Another important finding in Fig. 1 is the deformation of the band shapes. This is not the situation which would be expected from anomalous dispersion of refractive index of the surface film. In the system used in the present work, however, the incident beam is not parallel and is always accompanied by a divergence of the angle of incidence. A divergence of about 16° was determined in the present case. Judging from Fig. 2 the band deformation was probably caused to some extent

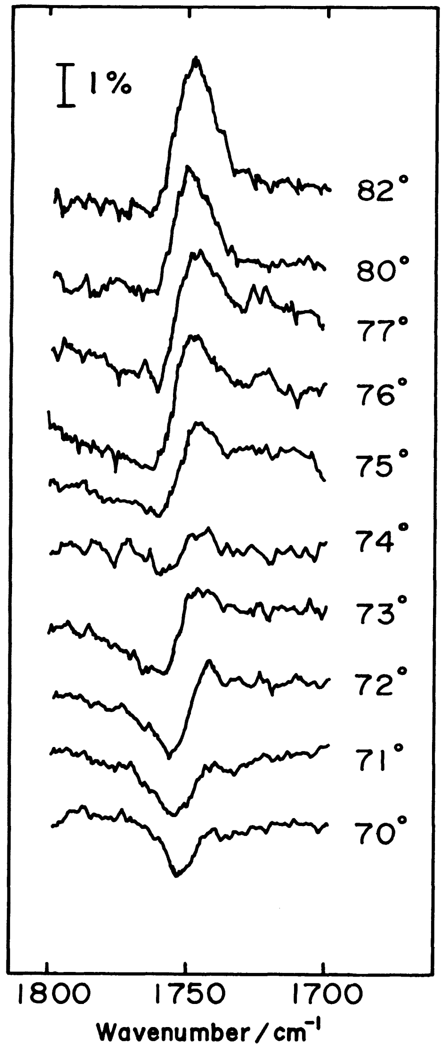

Fig. 1. The change in IRRAS spectrum as a function of the angle of incidence for the C=O stretching of a PVAc film on silicon. Increase in reflectivity is upward relative to background.

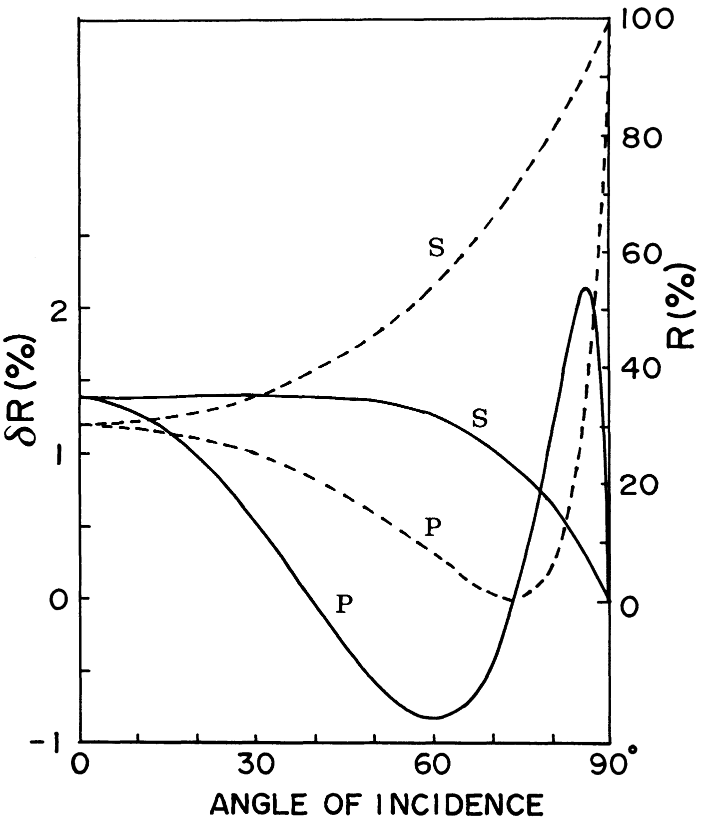

Fig. 2. The reflectivity of a bare Si at $\lambda = 5.7\ \mu m$ (R,---) and the change in reflectivity (δR,—) caused by the presence of an absorbing PVAc film 80 nm thick on Si, as a function of the angle of incidence for parallel (P) and perpendicular (S) polarizations. The optical constants used are $\hat{n} = 1.4 - 0.5i$ for PVAc; $\hat{n} = 3.42 - 0.0i$ for Si.

by a mixture of larger and smaller angles of incidence.

Figure 2 can also be used as a guide in determining the optimum angle of incidence for the IRRAS measurement. A conclusion that can be drawn from Fig. 2 is that with angles of incidence above 80°, preferably at 86°, the reflectivity change and therefore spectral intensity is greater for p-polarized radiation than for s-polarized radiation.

Shown in Fig. 3 for comparison are the conventional IRRAS spectra and polarization-modulation IRRAS spectra, both obtained from the same samples at the same angle of incidence of 80°. The bands at 1744 and 1256 cm^{-1} are assigned to the C=O stretching and the C-O-C antisymmetric stretching vibrations, respectively. The 1370 cm^{-1} band due to the CH_3 and/or CH_2 deformation is barely distinguished from the background. However, it is evident that the S/N ratio of the spectra is remarkably improved by the use of the modulation technique. This fact indicates that the polarization-modulation technique can be applied in obtaining the IRRAS spectra of thin films on silicon and other semiconductor surfaces. As is shown in Fig. 3, the intensity of the peaks in-

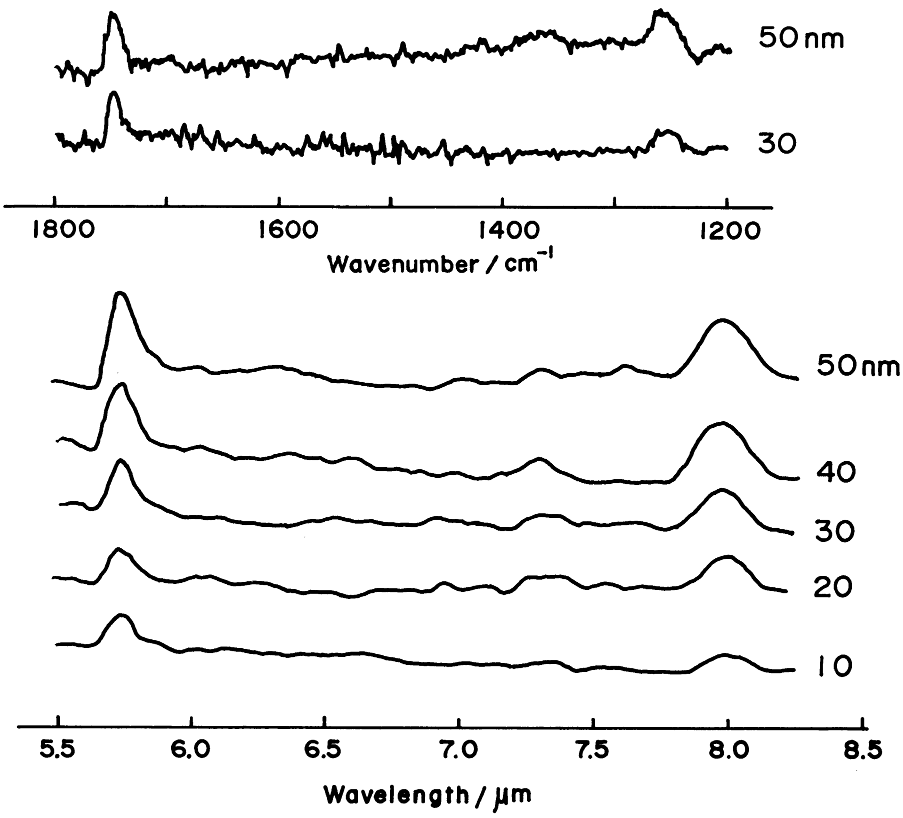

Fig. 3. Polarization-modulation IRRAS spectra of PVAc films on silicon having thicknesses written in the figure; upper spectra were measured with the conventional double-beam method. Increase in reflectivity is upward relative to background.

creases in rough proportion to the increase in film thickness, in conformity with the MacIntyre-Aspnes model. Moreover, it was found that the spectrum of a PVAc film on Si is lower in intensity by a factor of 1/50 than the band intensity from the film of the same thickness, which was, however, deposited on a Ag substrate. This result can be quantitatively accounted for by using values of δR calculated for Si and Ag.

In conclusion, IRRAS spectra of thin films on Si surfaces can be obtained by using p-polarized radiation, provided the optimum angle of incidence is used. Furthermore, the use of polarization-modulation technique enables us to obtain good spectra of thin surface films on Si and probably other semiconducting materials. This technique should be feasible for the investigation of opaque semiconductor surfaces in particular.

This work was supported by Toray Science and Technology Grants, to which thanks are due.

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(Received May 6, 1983)