Optical absorption in amorphous Si films at high pressure

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We report the pressure-dependent optical absorption in the fundamental edge region of amorphous silicon prepared by sputtering and glow discharge methods. For pressures up to 20 kbar we find a negative pressure coefficient of about 1×10^{-6} eV/bar for the isoabsorption energies. In a higher range of pressure, starting with pressures of about 50 kbar, we observed irreversible red shifts in the absorption curves.

INTRODUCTION

Optical experiments at hydrostatic pressures in the range 0-10 kbar have long played a very useful role in revealing the details of the band structure of crystalline semiconductors. In particular, measurements of absorption and reflectance on a large number of materials have led to the formulation of a well-known empirical rule governing the pressure dependence of band-energy extrema. Simply stated, the rule is: Pressure coefficients of the energy extrema of zinc-blende semiconductors depend principally upon the identity of the symmetry point (Γ , X, L, etc.) associated with the extremum, and very little upon the identity of the actual component materials.¹

According to this rule, for instance, the Γ points of the conduction-band minima located at the center of the Brillouin zone have pressure coefficients (with respect to the valence-band Γ -point maximum) which are always positive and of a magnitude $dE/dp \approx 10^{-5}$ eV/bar. On the other hand, X points or points near X (at the zone boundary in the $\langle 100 \rangle$ direction of k space) have negative pressure coefficients about an order of magnitude smaller than Γ points. Finally, L points at the zone boundary in the $\langle 111 \rangle$ direction have positive pressure coefficients about half as large as those at Γ .

Since this rule holds without serious exception in all crystalline semiconductors of the zinc-blende type, it can be extremely useful as a tool with which to identify incompletely known band structures in new materials. In particular, with respect to amorphous materials, optical investigations at high pressures can perhaps furnish the answer to the following question: For those amorphous materials that are characterized by an absence of long-range order, and a retention of short-range order (as is the case for the tetrahedrally bonded amorphous semiconductors) what remains, if any,² of the crystal band structure which can be identified by the pressure dependences in an optical absorption experiment?³

There are two circumstances which led us to

consider amorphous silicon (a-Si) as a likely candidate for this type of investigation. The first is that among the well-studied crystalline semiconductors, such as Si, Ge, GaAs etc., only in the case of Si are the X, L, and Γ points of the conduction band well separated (on the scale of the fundamental band gap). Therefore, in a-Si, simple optical measurements have the best chance to be free of ambiguity.² The other circumstance is that recent work by Connell and Paul³ seemed to indicate that the pressure coefficient of the fundamental absorption in a-Si is positive, albeit still small, whereas it is known to be negative in the crystalline state. Since the coefficient is so small, it seemed desirable to repeat those measurements over a wider range of pressures than was available to Connell and Paul.

EXPERIMENTAL

The diamond anvil cell has been employed in this work to obtain the optical data at high pressure. This device in one form or another has been in use in a number of laboratories in recent years to achieve pressures previously requiring much more bulky apparatus. When used in a Bridgman configuration with a metal gasket and fluid interposed between the anvils, the cell is uniquely suitable for achieving with relative ease quasi-hydrostatic pressures well in excess of 100 kbar. A particularly valuable innovation, first introduced at the National Bureau of Standards, was the ruby fluorescence method of measuring the pressure, which provided a reproducible pressure scale of unprecedented convenience.⁴ However, weighing these undoubted advantages against older methods must be the fact that the size of the diamond anvils and the overall scale of the apparatus necessarily restrict the sample size to about 0.1 mm. Because of this latter restriction, the cell was initially used principally for x-ray investigations and the direct observation of phase changes, and only rarely for straightforward optical investigations. We found, however, that with due regard to the

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FIG. 1. Optical system used in this experiment. Beam splitter is removed during the measurement of the optical absorption. It is needed only when measuring the pressure with the ruby R lines.

design of optical components, and the use of the best available detectors and light sources, the small sample size is not always an insurmountable impediment, and the cell may be used in conventional fashion to obtain transmission, reflection, and luminescence spectra at high pressures.⁵

Figure 1 illustrates the optical setup. The light source is a quartz halogen lamp or a Xe highpressure arc lamp which is focused on an aperture whose diameter is slightly smaller than that of the sample in the cell. The cone of radiation leaving the aperture is returned to the desired portion of the cell and brought to a sharp focus by means of a large spherical mirror equipped with x, y, z, micrometer adjustments. Because the aperture is nearly at the center of curvature of the spherical mirror (the magnification is almost 1:1), the resultant image in the cell proper is free of coma and spherical aberration. The measurement consists of alternately passing the radiation first through the sample and then through the empty portion of the cell, thus compensating for the reflection losses at the diamond-air and the diamondliquid interfaces. The transmitted radiation is collected by a reflecting objective (which eliminates chromatic effects) mounted at the end of a microscope tube. The latter forms part of a conventional assembly equipped with the usual adjustments for focusing and directly viewing the sample with ocular evepieces. Except when viewing the sample, the radiation is focused onto the end of a light fiber bundle whose other end terminates at the entrance slit of a spectrometer. The spectral range covered by the apparatus is 0.6-4.5 eV with special fibers required for the ir and uv ranges.

Two different type of samples were used in this study. A sputtered film about $10-\mu$ m thick was prepared by rf sputtering from a nominally intrinsic silicon cathode onto a room-temperature copper substrate. Flakes of freely supported *a*-Si peeled off the substrate and were used for the optical measurements as well as for x-ray diffraction analysis which confirmed the amorphous state of the film. Similar flakes $3-5-\mu$ m thick of *a*-Si from a glow discharge⁶ of silane were kindly supplied to us by the Marburg group. These samples were grown at ~250 °C, and were originally on quartz substrates.

RESULTS

Our first results were obtained on sputtered *a*-Si. This material was prepared in a manner entirely similar to those of Connell and Paul,³ but, as we shall see, our conclusions regarding the optical properties at high pressure differ. This material tended to exhibit a pronounced absorption tail to-wards low energies. In analyzing the data it was necessary to exercise extreme care to correct for changes in the reflection losses at the sample-liquid interface. It will be recalled that under appropriate conditions [viz., $R^2e^{-\alpha d} \ll 1$, $(\alpha\lambda/4\pi)^2 \ll n^2$, where *R* is the reflectance, α the absorption coefficient, and *n* the refractive index of the sample whose thickness is *d*], the absorption co-



FIG. 2. Variation of the refractive index of the alcohol medium with pressure. These data are used to calculate the factor $(1-R)^2$, also shown.

efficient can be found from an expression

$$I/I_{o} = (1 - R)^{2} e^{-\alpha d}$$
 (1)

which is a simplified form of the exact Barnes and Czerny formula. Here I/I_0 is the transmission ratio, which we measured, and R is the actual reflectance of the sample *in the medium*, which we inferred as follows: To a sufficient approximation

$$R = [(n_{\rm Si} - n_{\rm lig})/(n_{\rm Si} + n_{\rm lig})]^2, \qquad (2)$$

and it is obvious that this quantity must decrease steadily and substantially as the density of the liquid and hence, its refractive index, increase with pressure. We calculated the pressure dependence of the refractive index of the liquid (which consisted of a mixture of methyl and ethyl alcohol) from the known density vs pressure data, employing the Clausius-Mossotti equation to relate the density to the refractive index. Implicit in this procedure is the assumption that the molecular polarizability is independent of density. This turns out to be an excellent approximation as we later verified by measuring the absolute reflectance of a diamond-liquid interface at various pressures. The refractive index together with the factor $(1-R)^2$ is plotted in Fig. 2. It is clear that failure to take this pressure dependence into account correctly would lead to erroneous conclusions regarding small changes in α .

The calculated values of α vs $\hbar \omega$ for a number of pressures are shown in Fig. 3. The principal result of these measurements on a sputtered sample of *a*-Si is that the shift in the band edge that was obtained from isoabsorption values is negative with increasing pressure, having everywhere a value

 $\Delta E_{e}/\Delta P \approx -(1\pm0.5)\times 10^{-6} \text{ eV/bar}$.

This value is very similar in magnitude and the same in sign as what has been found for crystalline

Si. Although it differs in sign with what is reported by Connell and Paul, namely, $+0.25 \times 10^{-6}$ eV/bar, a negative sign is not ruled out by the typical experimental uncertainty usually encountered at the low pressures available to them. We estimate about a $\pm 50\%$ uncertainty in our coefficient, mainly due to the corrections required by Eq. (2).

The range of pressure covered in the measurements of Fig. 3 is not sufficiently great to say whether the shift is linear with pressure, nor whether there are any irreversible changes occurring, though we made some attempt to ascertain the latter.

These points were investigated for the a-Si films obtained from a glow discharge of silane gas. Conditions in this experiment were more nearly "ideal" in the sense that it was possible to span a rather wide range of pressures. Two samples were used. The first was employed in a series of measurements where the pressures were progressively increased from 0 to 69 kbar. It was in the course of analyzing these data that we were led to the conjecture that there may be irreversible changes occurring in the material as it is carried into the high-pressure ranges. A second experiment was then performed which confirmed this conjecture.

Fig. 4 shows the absorption data on the first sample of silane-discharge-grown *a*-Si. We show only the data in the strongly absorbing region. The sample was about $5-\mu m$ thick, and its full spectrum covered the energy range 0.6-2 eV. It exhi-



FIG. 3. Results of measurements on a sputtered sample of a-Si. Shown are the relative absorption data after correction for the pressure-dependent effect of the sample liquid interface.





bits in the lowest energy range the usual well developed set of interference fringes whose finesse very nearly correspond to the ideal zero-absorption value expected from the Fabry Perot formula for a plate in an alcohol medium. At 1.5 eV, which is where Fig. 3 begins, the fringe amplitude and finesse is already sufficiently degraded so that a simple averaging of maxima and minima sufficed to extract the absorption coefficient. In the region of highest absorption ($\alpha d \approx 7$), the tendency of the data to flatten must be regarded as instrumental, due undoubtedly to the effects of scattered radiation reaching the detector.

The data of Fig. 4 is used to make an isoabsorp-



FIG. 5. Isoabsorption plot of data of Fig. 4 for the value $\alpha d = 4$. Plots for other values of αd behave similarly.

tion plot for the value $\alpha d = 4$, as shown in Fig. 5. From this figure, it is immediately apparent that although the pressure coefficient in the low-pressure region is indeed small and of order -1×10^{-6} eV/bar it shows a tendency to accelerate to much larger values at pressures higher than ~20 kbar. It is this sort of behavior which suggested that irreversible effects may be setting in.

Another sample of the same material was therefore employed in a series of measurements whose precise purpose was to look for irreversibility by



FIG. 6. Isoabsorption data for a sample undergoing excursions into the high-pressure region followed by relaxation to atmospheric pressure. The arrows show the sequence of pressures, the points the actual values of the isoabsorption energies as a function of pressure. The irreversible effects evidently grow larger as the terminal pressure is increased. Sample is a second piece of the same film described by the data in Figs. 4 and 5.

going up and down the pressure range. The result was a family of curves not unlike those in Fig. 4. However, when the isoabsorption data was plotted in the manner of Fig. 5, it became obvious that release of the pressure from some high value does not reproduce the initial state. These data are shown

sample by a series of arrows.

DISCUSSION

in Fig. 6 which traces the pressure history of the

The results presented above give us only rudimentary information about the pressure-dependent optical absorption in a-Si. First we infer by an isoabsorption analysis a negative and, on the scale of the zincblende structure crystals, small dE/dP. This finding is common to the 1.0-1.1 eV rising absorption range of the sputtered sample and to the corresponding 1.7-1.8-eV range of the silane glow discharge samples. In the sputtered case, the absorption process is almost certainly not intrinsic, but most likely associated with defects, e.g., dangling bonds.² For the silane glow discharge films, the dangling bond absorption is believed to be negligible near 1.0-1.1 eV and the observed edgelike absorption we observe at 1.7-1.8 eV may involve intrinsic processes⁶ but even here we do not know that for sure. It is strange that we observe $dE/dP \approx -1 \times 10^{-6}$ eV/bar for both cases. Furthermore, the $dE/dP = -1 \times 10^{-6} \text{ eV/bar}$ value is, in zincblende structure crystals, associated with transitions to the conduction-band minima along the reciprocal space $\langle 100 \rangle$ direction, a direction of no special or identifiable significance for amorphous structures. At this point, we do not wish to speculate further on the meaning of this result, particularly in light of the irreversible effects discussed below.

We have found, for the silane glow discharge films, that the rise in absorption shifts irreversib-

ly to the red after the application and release of pressures of 50 kbar or more. This raises the question that the observed dE/dP is due in part to structural changes and not at all analogous to the similar dE/dP of crystal silicon. It is not surprising that there may be a pressure-induced relaxation of the amorphous silicon structure. We know that a-Si is permeated with voids,² probably of the size of 2 to 5 atom vacancies.⁶ Glow discharge films, even if free of dangling bonds, may not be void-free. The voids almost certainly contain hydrogen on the dangling bonds that preclude their observation by the normal methods of electron spin resonance or optical absorption. Thus the applied pressure may be redistributing the atoms in and near the voids in an irreversible fashion that shows up as the extra absorption when the pressure is released. It is important in this connection to note that pressure-induced partial recrystallization is an unlikely explanation of the irreversibiliy, since this would produce decreased overall absorption in the 1.7-1.8-eV energy range when the pressure was released.

CONCLUSIONS

In summary, we have found that the measured pressure coefficients as obtained from the isoabsorption levels in our samples of a-Si are negative and of order of magnitude 10^{-6} eV/bar. For pressures exceeding about 50 kbar we have observed irreversible red shifts of the same order of magnitude in those samples which we were able to examine in this pressure regime.

ACKNOWLEDGMENTS

We thank Dr. R. Fischer and Dr. D. Engemann of Marburg University for supplying the glow discharge films used in this study.

¹For a review of this work see, for instance, W. Paul, in *The Optical Properties of Solids*, edited by J. Tauc (Academic, New York, 1966), p. 257.

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