

Electroreflectance Observation of Internal Photoemission in InSb

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(Z. Naturforsch. **24 a**, 1320–1322 [1969]; received 16 June 1969)

Herrn Prof. Dr. H. GOBRECHT zum 60. Geburtstag gewidmet

Electroreflectance is being used to determine the character of InSb surface layers exposed to uv irradiation. On n-type surfaces, such irradiation induces a charge transfer from band states into trapping states in the oxide layer, and the surface converts to p-type. Relevant parameters of this charge transfer such as threshold energy and rate of thermal recovery are determined for different surface conditions and temperatures. The convenience of electroreflectance as a continuous monitor of surface processes in InSb is pointed out.

On a qualitative basis, it has long been known that the surface properties of InSb can be changed by irradiation with light¹. The incident light renders n-type surfaces unstable by converting them into p-type layers through a photo-induced charge transfer. Using the field-effect of the surface conductance, MUELLER and JACOBSON² demonstrated this conversion and postulated a model in which photons of sufficient energy lift electrons from band states over the potential barrier between InSb and its oxide. These electrons get trapped in localized states in the forbidden gap of the oxide, thereby converting an original n-type layer at the interface into a p-type layer that persists until thermal re-emission into the band restores the previous situation.

Since this early work, the use of InSb in semiconductor technology has considerably increased and the photosensitivity of surfaces is of concern in the processing of this material. Quantitative measurements of the effect are desirable, performed with a method easier to use and of wider range of application than the field effect technique³. We report here measurements of the electroreflectance spectrum of InSb under variable surface conditions that establish the photo-induced charge transfer quantitatively and recommend electroreflectance as a convenient optical technique for further study of this effect.

The potential of electroreflectance in the determination of semiconductor surface parameters was first recognized in the field-effect version of the technique³. GOBRECHT and co-workers⁴, in a num-

ber of careful experiments, expanded this aspect of electroreflectance into investigations of the semiconductor-electrolyte interface.

Unlike most other surface measurements, electroreflectance does not monitor a transport phenomenon based on an excess of carriers in the surface. It depends rather on the surface field, sensitively determining the reversal of the field direction at the flat band condition by a sign reversal of the optical response⁵. Based on this established electro-optical surface phenomenon, the conversion of an n-type surface into a p-type layer through photons of sufficient energy can conveniently be followed by observing the sign of the electroreflectance response.

The spectra shown in Fig. 1 were both measured at 300 K on the same sample of 10^{17} cm^{-3} N InSb which had been polished, etched in 2.5% Br_2 :methanol, and coated with 150 Å of Al_2O_3 . This layer served as the dielectric of a metal-insulator-semiconductor (MIS) structure, completed on top by a semitransparent Ni-electrode. The spectra were taken under two different surface conditions as adjusted by +1.0 V bias for the upper, and –0.5 V bias for the lower trace.

Immediately apparent is the similarity of the spectra in one spectral region and their striking difference in others. The strong structure around 1.9 eV consists of a down-up sequence in the upper trace that is almost exactly inverted in the lower trace. Such an inversion of sign, as established by previous field-effect controlled studies^{3,5}, indicates

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¹ J. D. VENABLES and R. M. BROUDY, *J. Electrochem. Soc.* **107**, 296 [1960]. — G. K. EATON, R. E. J. KING, F. D. MORTEN, A. T. PARTRIDGE, and J. G. SMITH, *J. Phys. Chem. Solids* **23**, 1473 [1962].

² R. K. MUELLER and R. L. JACOBSON, *J. Appl. Phys.* **35**, 1524 [1964].

³ B. O. SERAPHIN, *Surface Sci.* **8**, 399 [1967]; **13**, 136 [1969].

⁴ H. GOBRECHT, M. SCHALDACH, F. HEIN, R. THULL, and H. J. KOS, to be published. — H. GOBRECHT, R. THULL, F. HEIN, and M. SCHALDACH, to be published.

⁵ B. O. SERAPHIN, R. B. HESS, and N. BOTTKA, *J. Appl. Phys.* **36**, 2242 [1965].



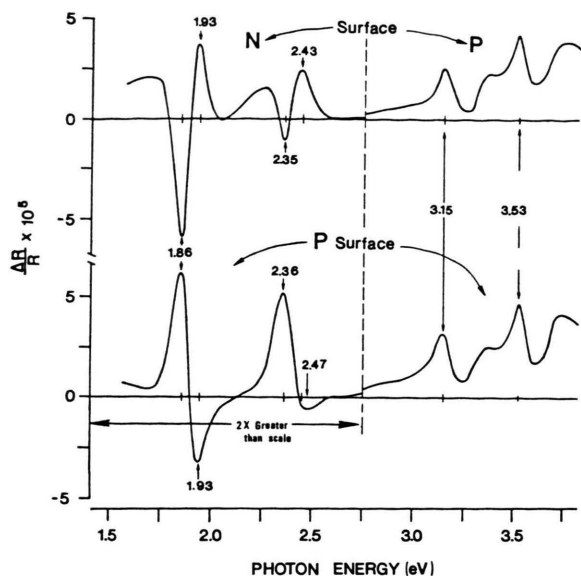


Fig. 1. Electroreflectance spectrum of InSb 10^{17} cm^{-3} N recorded at 300 K in the MIS configuration. Below about 2.5 eV, the reflecting surface of the upper trace (+ 1.0 V DC bias) was n-type and was converted to p-type at higher energies due to internal photoemission. In the lower trace (- 0.5 V DC bias) the surface was p-type over the entire spectral range.

a change in sign of the surface potential. We can conclude that the upper trace taken with a more positive bias than the lower, represents an n-type layer and the lower trace a p-type layer, the flat band condition being passed in between. The same argument applies to the structure at 2.4 eV.

The strong dissimilarity of the two traces is not present in the range of larger photon energies. The group of peaks around 3.15 and 3.53 eV, previously observed in the electroreflectance spectrum of InSb⁶, is identical for both positive and negative bias. Since the surface field of the potential barrier generates the response at small and large photon energies alike, we must suspect an influence of the sampling light on the surface potential.

This can indeed be demonstrated by completing the spectral scan of the upper trace to about 4.0 eV, and then quickly returning to 1.86 eV where the response was negative at the outset of the scan. The return now finds the response to be positive, indicating a sign inversion of the surface layer under the influence of the incident light during the scan. The magnitude of this positive response decreases, changes sign and finally returns to its original negative magnitude after several minutes.

⁶ M. CARDONA, K. L. SHAKLEE, and F. H. POLLAK, Phys. Rev. **154**, 696 [1967].

In order to determine the threshold of this photo-induced inversion of the surface sign, the sample was sequentially exposed to light pulses of equal length, but increasing photon energy. No correction was made for the change in photon flux with energy and the measurement was taken at 80 K. In between pulses, the surface type was determined by recording sign and size of the calibration peak now located at 1.96 eV instead of 1.86 eV at room temperature. A change in sign and size of this calibration peak indicated that the preceding light pulse had changed the surface layer.

The results are shown in Fig. 2. Light pulses of up to 2.5 eV photon energy are relatively inactive with respect to a conversion of the surface layer. Beginning at 2.5 eV and increasing in a rather sharp threshold, photons of larger energy cause the surface layer to invert to p-type (in between pulses, the surface was restored to n-type, as will be shown below). Since the photon flux decreases towards larger photon energies, a normalization with respect to the flux would make the threshold even steeper.

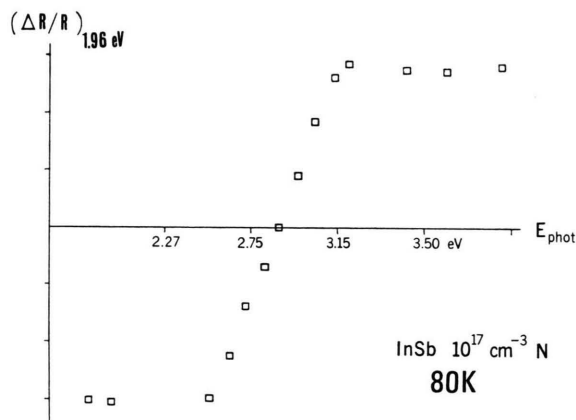


Fig. 2. Sign and magnitude in arbitrary units of the peak at 1.96 eV, indicating type and strength of the surface space-charge layer, after sequential exposure of an n-type surface to light pulses of equal length, but increasing photon energy E_{phot} . The steep rise and sign inversion around 2.8 eV indicate the threshold energy for internal photoemission of electrons from band states into trapping levels.

The photo-induced charge transfer is followed by a gradual re-emission of the charge that restores the previous surface condition. The time dependence of this re-emission was taken into account in order to make the experiment meaningful. At room temperature, the charge escape back into the band was accomplished within tens of seconds and the

"half-life" of the converted surface determined the charge transfer rate of the previous excitation.

A number of detailed studies conducted at liquid-nitrogen temperature further clarified the distribution of charge and potential on either side of the semiconductor-oxide interface. The sign of the 1.96 eV calibration peak indicated the type of the semiconductor surface layer throughout the various phases of these studies. These results can best be described in terms of the space-charge region (band states) on one, and of trapping states on the other side of the interface. We must conclude that the system can apparently exist in two different states that are characterized by their different sensitivity toward uv light and changes of DC bias.

We best visualize the results by going through the following cycle. Let us assume a freshly etched surface ordinarily p-type in InSb. Such a surface readily responds to changes in DC bias. In particular, small positive values of the DC bias pull the surface through the flat band condition over to the n-side.

If we irradiate such a surface with uv light while it is on the p-side, we observe little change. After the light is switched off, this p-type surface is still as "soft" with respect to changes in DC bias as before the irradiation. This insensitivity can result from the potential barrier at the interface in this particular configuration, or the absence of electrons in the surface layer can be credited.

The result is quite different if the uv light hits an n-type surface obtained by pulling the original, soft p-type surface through the flat band condition. The light now transfers electrons over the barrier into trapping states and the distribution of charge and potential is severely changed. The p-type surface resulting from the irradiation is "hard" with respect to changes of its quiescent potential, requiring large values of the DC bias.

We can close the cycle by applying a large negative bias to such a photo-inverted hard p-type layer. The trapping states are cleared of electrons and a p-type layer results that is soft again and can readily be swung over to the n-side by a small positive bias.

All of these effects are consistent with the basic model of a dielectric layer with trapping states at the InSb surface and a threshold of the photoemission which depends upon the properties of this layer². This is probably an unavoidable oxide layer. Any additional coating strongly influences the barrier height and therefore the threshold energy.

We found surfaces anodically oxidized to have a threshold considerably lower than samples carrying an Al₂O₃ dielectric. The position of the nearest bands in the dielectric with respect to the Fermi level as well as the spatial distribution of the trap-generating impurities in the oxide and dielectric apparently determines the threshold for conversion. We then have the following picture. Electrons, once lifted over the interface barrier into trapping states, and thus immobilized, act as a screening electrode in front of the positive field electrode causing a depletion of electrons in the space-charge region.

After the photon energy is lowered below threshold, thermal excitation is sufficient at room temperature to clear the traps and return the electrons to band states. At 80 K the thermal escape is extremely slow and lowering of the barrier by strong negative bias is required to raise the rate of return into the band states.

The optical technique used in this study represents a convenient and powerful tool to quantitatively determine the parameters of an InSb surface while the conditions are being changed. Conversion threshold and thermal escape rate can be determined as a function of surface preparation, adjacent material and impurity level in semiconductor and dielectric. Densities, energy position and lifetime of trapping states can continuously be monitored while a passivation layer grows. Optimum conditions with respect to environment, growth rate, applied bias, etc., can be adjusted accordingly.

It is interesting to note that internal photoemission provides an additional mechanism in our understanding of photoreflectance⁷. The reflectance modulation observed in this technique by the periodic irradiation of the reflecting surface with strong light pulses would for InSb in part result from a modulation of the surface field by the photo-induced charge transfer into trapping states. Although many of these states would stay populated for long periods of time compared to the modulation period, a fraction would be depopulated and cause a modulation of the surface potential.

Acknowledgements

We wish to thank N. BORTKA for several fruitful suggestions during the course of this work.

⁷ E. Y. WANG, W. A. ALBERS, and C. E. BLEIL, *Proc. Intern. Conf. II-VI Compounds*, Providence 1967 (ed. D. G. THOMAS), Benjamin Inc., New York 1967, p. 136. — R. E. NAHORY and J. L. SHAY, *Phys. Rev. Letters* **21**, 1569 [1968].