

Optical Detection of Surface States in Ge

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Measurements of field-effect-modulated optical absorption are presented for real surfaces of germanium. The spectra are taken for various values of the surface potential. They show a narrow peak at 0.438 eV (half-width ~ 0.01 eV) having maximum amplitude for a surface reduced potential $u_{s0} \simeq 1.8$ and a phase (with respect to the electric field) appropriate to transitions from a surface state to the conduction band. Evidence is given that such a transition is from a level $1.8kT$ above the mid-gap to the state Γ_2' of the conduction band. A much broader band is also found at smaller energies (0.39 eV); bands due to free-hole and free-electron absorption are also evident.

THE possibility of observing the optical spectrum of surface states by means of field-effect-modulated optical absorption has been recently demonstrated for Ge¹ and Si.² Monochromatic light totally reflected at the inner surface of a semiconductor becomes modulated when a normal electric field of frequency ν_0 is applied to the surface. In fact the external field periodically changes the position of the energy levels at the surface with respect to the Fermi level, thus varying their population and causing a modulation at frequency ν_0 of the absorption coefficient of the sample. The use of synchronous detectors allows a very great sensitivity to be reached: variations of light intensity of the order of 10^{-6} per single reflection are easily detected.

We present here evidence of a well-defined optical transition from a fast surface state situated near the midgap of germanium to states around the point Γ_2' of the conduction band at $\mathbf{k}=0$.

In our experimental setup, light was totally reflected 20 times on the (111) surface of 20 Ω cm *n*-type germanium 0.5-mm thick, to which an ac field of 4×10^4 V/cm and frequency from 40 to 500 cps was applied. Figure 1 shows the signal at frequency ν_0 (normalized for constant intensity of light) as a function of the energy of the photons for a "real" surface, etched in white etch and dried for several days. Signals in phase with the electric field are shown as positive in the figure. The various curves refer to different values of the surface reduced potential $u_{s0} = e\phi_{s0}/kT$, obtained by changing the ambient gases (through various O₃-O₂, O₂, O₂-H₂O mixtures). The surface potential was measured by conventional field-effect techniques,³ the "parabola" being observed on an oscilloscope during the entire run

so that an eventual drift of u_{s0} could be easily compensated.

The spectra of Fig. 1 seem to depend on surface treatment (for example, band β of Fig. 1 disappears when the surface is exposed for several hours to wet N₂); they do not vary with the frequency of the applied field in the range considered.

In principle, field-effect-modulated optical absorption can be due to the following processes:

- (i) transitions from the valence band to an empty surface level;
- (ii) transitions from a filled surface level to the conduction band;
- (iii) modulated free-hole absorption in the surface layer;
- (iv) modulated free-electron absorption in the surface layer.

The modulated shift of the absorption edge caused by the Franz-Keldysh effect can also contribute to the signal.⁴ Signals due to (i) and (iii) are in phase with the ac field,⁵ while signals due to (ii) and (iv) have the opposite phase.

From the curves of Fig. 1 one sees that when the surface is strongly *p*-type (as in curve A), modulated free-hole absorption in the surface layer predominates, giving rise to a broad band at 0.375 eV identical with that observed in the absorption spectra of bulk *p*-type Ge.⁶ For a strongly *n*-type surface, on the other hand, the signal is predominantly due to modulated free-electron absorption (curve G) and approximately follows a λ^2 law. For intermediate values of u_{s0} , the curves (B to F) clearly show a narrow peak (β) at 0.438 eV (half-width 0.01 eV) and a broad band (α)

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¹ G. Chiarotti, G. Del Signore, A. Frova, and G. Samoggia, *Nuovo Cimento* **26**, 403 (1962).

² J. N. Harrick, *Phys. Rev.* **125**, 1165 (1962).

³ H. C. Montgomery and W. L. Brown, *Phys. Rev.* **103**, 865 (1956).

⁴ M. Chester and P. H. Wendland, *Phys. Rev. Letters* **13**, 193 (1964); A. Frova and P. Handler, *ibid.* **14**, 178 (1965).

⁵ The field is assumed conventionally positive when the field effect electrode is positive. In determining the phase of the signal it should be taken into account that an increase in the probability of a transition gives rise to a decrease of the light reflected by the surface.

⁶ H. B. Briggs and R. C. Fletcher, *Phys. Rev.* **91**, 1342 (1953).

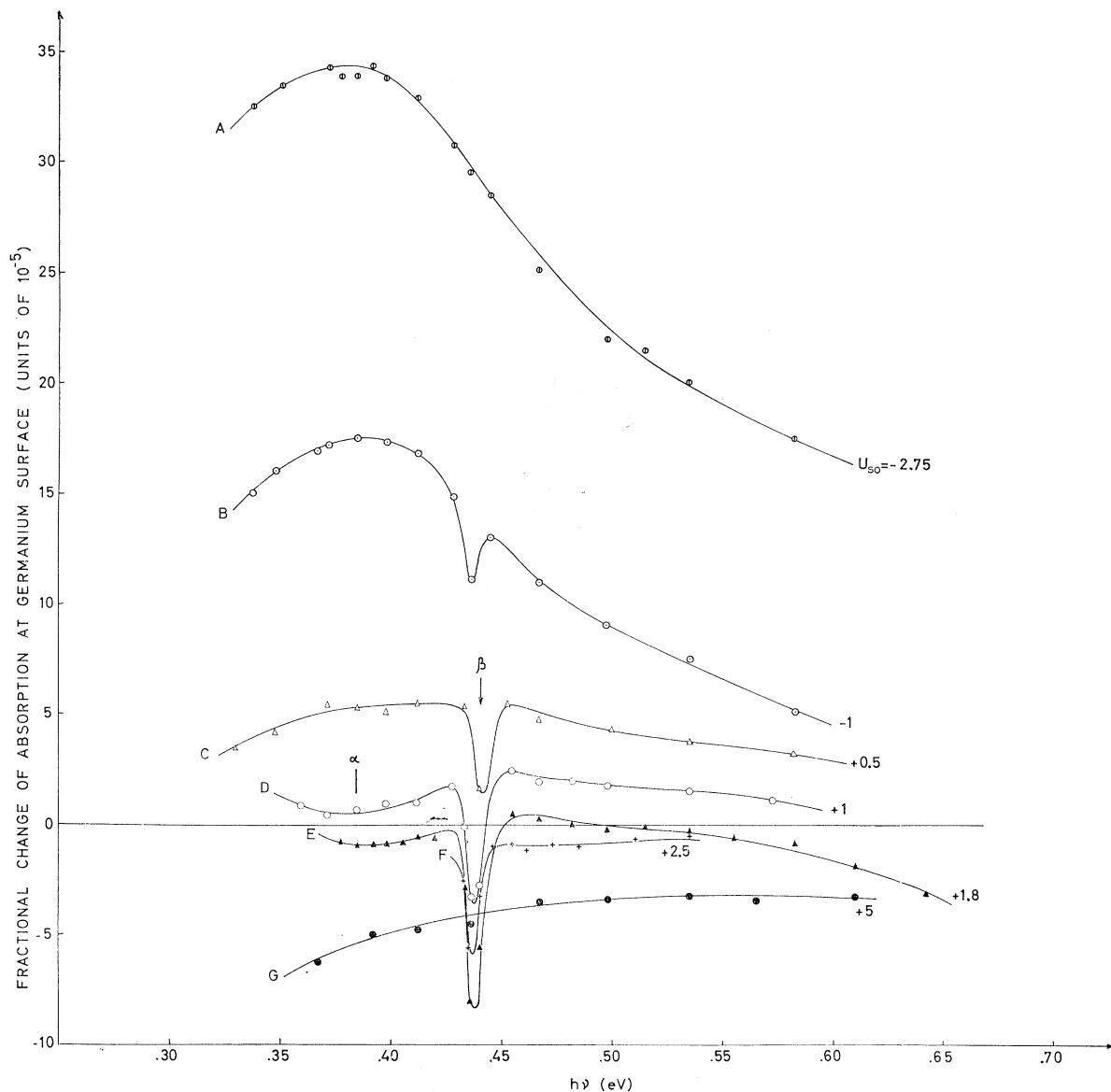


FIG. 1. Field-effect-modulated optical absorption in Ge. The various curves (normalized for constant intensity of incident light) refer to different values of surface potential. Peak β has maximum amplitude for $u_{s0}=1.8$.

near 0.39 eV, with phases appropriate to transitions of type (iii), i.e., from an occupied surface level to the conduction band. If this interpretation is correct, the peaks should have maximum amplitude when the states cross the Fermi level at the surface. In fact one sees from the curves of Fig. 1 that the peak β has a sharp maximum for $u_{s0}=1.8$. Assuming that the transition involved is to states of the conduction band near the point Γ_2 , at $\mathbf{k}=0$, the energy of the threshold for the transition (i.e. the distance of the level from the bottom of the conduction band at $\mathbf{k}=0$) should be

$$h\nu = (\Delta E)_{\mathbf{k}=0} - \frac{1}{2}\Delta E - e(\phi_{s0})_{\max},$$

where $(\Delta E)_{\mathbf{k}=0}$ and ΔE are, respectively, the direct gap

(0.803 eV)⁷ and the indirect gap (0.665 eV).⁸ One then finds for the threshold of the absorption peak β a value of 0.426 eV in agreement with the curves of Fig. 1. The present results therefore give evidence of the existence of a well localized surface level approximately $1.8kT$ above the midgap. In the same general scheme, the broad band α would correspond to a continuum of states centered approximately $3.5kT$ above the midgap.

Levels in the same energy range have been frequently reported in the literature⁹ from measurements of field

⁷ S. Zwerdling and B. Lax, Phys. Rev. **106**, 51 (1957).

⁸ G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957).

⁹ See, for example, A. Balzarotti, G. Chiarotti, and A. Frova, Nuovo Cimento **26**, 1205 (1962).

effect and various hypotheses on their origin have been made.^{10,11} Though the states detected in the present work depend on surface treatment, presently available information does not allow a definite conclusion as to their nature. Nevertheless, a few considerations follow directly from the experimental results: The spectrum of Fig. 1 does not show any evidence of transitions of type (i). For example, one would expect a signal, in

¹⁰ G. Dorda, Czech. J. Phys. **13**, 272 (1963).

¹¹ Y. F. Novotzky-Vlasov and A. V. Rzhano, Surface Sci. **2**, 93 (1964).

phase with the field, caused by transitions from the valence band to the level responsible for peak β , at energies around 0.37 eV. The absence of such a transition suggests that this level has a wave function of p -type symmetry which allows transitions to the states of the conduction band near $\mathbf{k}=0$ (s type) but not to those of the valence band (p type at $\mathbf{k}=0$). On the other hand, the fact that peak β is extremely narrow seems to suggest that only states of the conduction band very near $\mathbf{k}=0$ can be reached optically from the surface levels.

Theory and Observation of Intrinsic Surface States on Ionic Crystals

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A comprehensive theory of surface states on ionic crystals has been derived using Seitz's approach to bulk crystal energy states as a starting point. Surface ions are considered equivalent to bulk ions except for their reduced Madelung constant. The relationship of surface levels to bulk bandgap is expressed as a function of surface geometry and bulk material properties, and it is calculated using classical electrostatics for many surfaces of 46 halides, oxides, and sulfides. Symmetry arguments show that only for a checkerboard-like surface are the surface states symmetrically disposed about midgap. Numerical calculations show that one electron trap is formed from each surface cation and one hole trap for each surface anion; trap depths should be deepest for HgS, CdS, and ZnS; and for a (11 $\bar{2}$ 0) CdS surface the trap depths should be 0.2 to 0.4 eV, depending on the effective ionic charge assumed of 0.5 to 2.0. Intrinsic surface states were detected on the (11 $\bar{2}$ 0) surfaces of vapor phase grown insulating CdS single crystal platelets. Photoconductivity experiments (response time and thermally stimulated currents) indicate that these surface states function as traps for the photocarriers (electrons and holes) from the bulk.

I. INTRODUCTION

INTRINSIC surface states have been carefully investigated in the literature for metallic and covalent crystals,¹⁻¹¹ but surprisingly not for ionic crystals. There are, at present, only rough and qualitative theoretical criteria for predicting the nature of intrinsic ionic surface states and the experimental conditions necessary for their observation.¹²⁻¹⁴ Recently, evidence

has accumulated pointing towards the detection of intrinsic surface states on CdS.¹⁵⁻¹⁸

It is desirable, therefore, to formulate theoretical guide lines for predicting intrinsic-surface-state behavior for all ionic crystals and their crystal faces, to state the experimental criteria to be met in observing these states, and to report, in some detail, the intrinsic-surface-state properties inferred from CdS crystals.

Surface-state calculations for metallic and covalent crystals have been based essentially on either of two models. In the Tamm model, one assumes that the crystalline potential function is monotonic (all poles positive) and periodic, terminating at the surface plane. Surface states in the Tamm model are characterized by Bloch wave functions damped normal to the surface plane. In the tight binding model, the lattice is considered to be a collection of weakly coupled atoms filling half space. Surface states in this model are bulk states slightly modified due to the surface asymmetry. Other hybrid surface-state models have also been proposed. These models cannot be used for the ionic crystal because of two features. First, the monotonic

¹ I. Tamm, Physik Z. Sowjetunion **1**, 733 (1932).

² W. Shockley, Phys. Rev. **56**, 317 (1939).

³ E. T. Goodwin, Proc. Cambridge Phil. Soc. **35**, 205 (1939); **35**, 221 (1939); **35**, 232 (1939).

⁴ J. Bardeen, Phys. Rev. **71**, 717 (1947).

⁵ T. A. Hoffmann and A. Konya, J. Chem. Phys. **16**, 1172 (1948).

⁶ J. Koutecky and M. Tomasek, J. Phys. Chem. Solids **14**, 241 (1960).

⁷ T. B. Grimley, J. Phys. Chem. Solids **14**, 227 (1960).

⁸ M. D. Glinchuk and M. F. Deigen, Fiz. Tverd. Tela **5**, 405 (1963) [English transl.: Soviet Phys.—Solid State **5**, 295 (1963)].

⁹ J. Koutecky, J. Surface Sci. **1**, 280 (1964).

¹⁰ *Solid Surfaces*, edited by H. C. Gatos (North-Holland Publishing Company, Amsterdam, 1964).

¹¹ V. Heine, Phys. Rev. **138**, A1689 (1965).

¹² N. F. Mott and R. A. Gurney *Electronic Processes in Ionic Crystals* (Dover Publications, Inc., New York, 1964), p. 86.

¹³ P. P. Ewald and H. Juretschke, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C. S. Smith (University of Chicago Press, Chicago, Illinois, 1953), p. 82.

¹⁴ M. F. Deigen and M. D. Glinchuk, J. Surface Sci. **3**, 243 (1965).

¹⁵ P. Mark, J. Phys. Chem. Solids **25**, 911 (1964).

¹⁶ P. Mark, J. Phys. Chem. Solids **26**, 959 (1965).

¹⁷ P. Mark, Trans. N. Y. Acad. Sci. **27**, 946 (1965).

¹⁸ P. Mark, J. Phys. Chem. Solids **26**, 1767 (1965).