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Light-Induced Plasticity in Semiconductors*

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It has been found that light of wavelength between 2.0 and 4.0 μ, or shorter than 0.4 μ, decreases the hardness of the surface layer of *n*-type germanium by 10 to 60%. The softened layer extends to a depth of one to two microns. A similar but less intense effect was observed in *p*-type germanium and *n*-type InSb and InAs. On the other hand, *p*-type silicon seems to soften to a greater extent than germanium. The effect is proportional to light intensity and is affected by surface preparation.

AN analysis of the energy of dislocation in germanium, undertaken by Read,[1] revealed that it depends strongly upon the electron distribution within the dislocation. As light may produce a redistribution of the electrons in semiconductors, its effect upon the mechanical properties of these materials may be expected.

Such an effect which may be called a photomechanical effect, was indeed found by studying the microhardness of dark and illuminated semiconductor crystals. The hardness was measured with a standard Tukon microhardness tester, which employs a diamond Knoop indenter loaded with weights ranging from 1 to 100 grams. This type of indenter has such a shape that the length of the impression produced by it is 30 times its depth. It is therefore, best suited for measuring the hardness of thin surface layers. The following sources of light were employed in the experiments: a 150-watt Hanovia SH mercury lamp, two 140-watt Westinghouse reflector spot lamps, and a 60-kv copper-target x-ray tube.

The experiment itself was very simple. A polished and etched crystal was placed under the diamond indenter. When desired, the illuminating lamps were placed at a distance of 1.5 cm from the specimen. It should be added that the light source was never in contact with any part of the hardness tester during the experiment. (Wilson[2] noticed that vibrations caused by a light source mounted on the hardness tester can produce lower hardness readings.) Then the load was slowly applied and after 35 seconds lifted automatically. The longer diagonal x of the rhombic-shaped impression was measured under the microscope. The quantity $H=P/(7.028\times 10^{-2}x^2)$, where P is the applied load in kilograms, and x is measured in millimeters, is the so-called Knoop hardness number. This number is directly proportional to the yield stress of the material,[3] and thus can be used as a convenient indicator of the deformability of the material.

The photomicrographs in Fig. 1 show the relative sizes of Knoop impressions made on various semiconductors with and without illumination. As the length

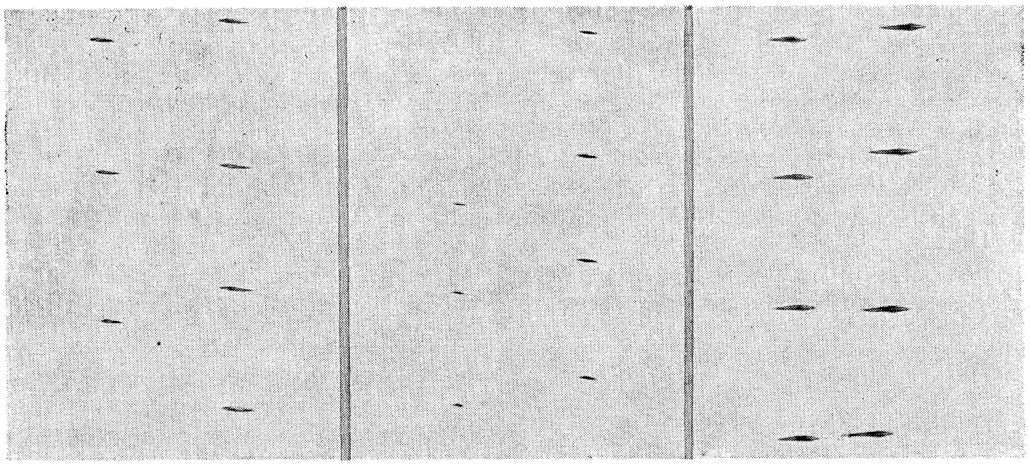
(a) (b) (c)

FIG. 1. Knoop impressions on (a) *n*-type germanium crystal, obtained with a load of 2 grams, 1000×; (b) *p*-type silicon crystal, 5-gram load, 400×; and (c) InSb, 5-gram load, 400×. All impressions in the left-hand rows were obtained in darkness; those at the right, under illumination of two 140-watt reflector spot lamps.

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* Supported by the Office of Naval Research.

[1] W. T. Read, Jr., Phil. Mag. **45**, 775 (1954).

[2] R. Wilson, Ph.D., Dissertation, University of Cambridge, England, 1952 (unpublished).

[3] D. Tabor, Brit. J. Appl. Phys. **7**, 159 (1956).

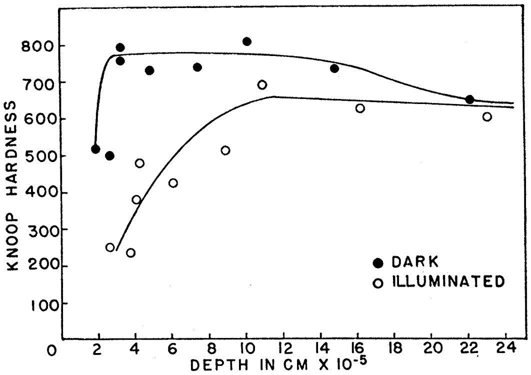

FIG. 2. Knoop hardness as a function of the distance from the surface of a germanium crystal containing about 2.3×10^{13} cm^{-3} ionized impurities. ● dark hardness; ○ hardness under the illumination of two 140-watt reflector spot lamps.

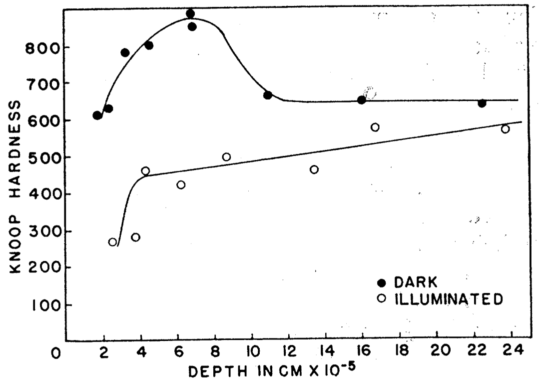

FIG. 3. Knoop hardness as a function of the distance from the surface of a germanium crystal containing 3.0×10^{14} cm^{-3} ionized impurities. ● dark hardness; ○ hardness under illumination of two 140-watt reflector spot lamps.

of the longer diagonal of the Knoop impression can be considered a measure of softness, it is obvious that the illuminated surface of these materials is very much softer than the same surface tested in darkness. Thus, the crystals whose hardness impressions are shown in Fig. 1 softened by 55% (Ge), 70% (Si), and 20% (InSb), when illuminated by ordinary lamps. A possible effect of crystallographic planes and directions upon the hardness of germanium crystals was also investigated. However, it has been found that the hardness number is independent of these variables within the limits of error of these measurements.

It has been found that the hardness of a layer only a few microns deep is affected by light. Figures 2 and 3 show the Knoop hardness numbers for dark and reflector-lamp illuminated germanium crystals plotted against the depth of penetration. The various depths were obtained by the application of different loads on the indenter. Figure 2 refers to an almost pure *n*-type germanium crystal containing 2.3×10^{13} cm^{-3} ionized donors (mostly antimony), and Fig. 3 to one containing about 3.0×10^{14} cm^{-3} such donors. These figures indicate that the effect is deeper in the purer crystal. The "dark hardness" curve passes through a pronounced maximum in intrinsic germanium, while in the less pure material (Fig. 3) this maximum is almost totally absent. Tests performed on a germanium crystal of intermediate concentration of impurities revealed a maximum less pronounced than in the very pure crystal and located closer to the surface. The very low hardness readings obtained for the few shallowest indentations, made with 1 and 2 gram loads, may be due to some vibrations present in the laboratory building. The observed photosoftening seems to be reversible, at least within the interval of time necessary for measuring hardness, about one minute.

As should be expected, the effect is directly proportional to the light intensity, because it falls off linearly with the square of the distance of the crystal from the light source.

An attempt was made to establish a relationship between the wavelength of the incident radiation and the decrement of hardness. When the light of a 140-watt reflector lamp was passed through a quartz filter transparent to light of wavelengths between 4.0 and 0.2 μ, a large softening effect (20–40%) was observed. When the quartz was replaced by a crown-glass filter, of transparence between 2.0 and 0.4 μ, the effect disappeared, indicating that the band of wavelengths in the infrared between 4.0 and 2.0 μ is responsible for it. A water filter was also tried. For this purpose, a water droplet was deposited on a germanium crystal of 3.0×10^{14} cm^{-3} concentration of ionized donors. This crystal softened by about 45% when a load of 5 grams and a source of unfiltered white light were used. Under the same conditions, but with the light passing through a water droplet on the surface, the magnitude of the effect was reduced to less than 10%; this is to be expected, because water is opaque to infrared radiation of the aforementioned wavelengths. However, when the reflector lamp was replaced by a mercury lamp, with the water droplet still on the surface of the sample, the germanium crystal softened by about 35%. This experiment indicates that, in addition to the band of effective wavelengths in the infrared, another one in the ultraviolet must exist. A few exploratory experiments made with Corning glass filters revealed softening of the germanium surface by radiation of wavelength shorter than 0.4 μ. The illumination of germanium crystals with radiation from a 60-kv copper-target x-ray tube produced no detectible effect.

In all these experiments great care was taken to eliminate the heating of the crystal surface during illumination. This was achieved by using thin films of mineral oil, acetone, or alcohol. All these liquids are transparent to the infrared radiation which causes the photomechanical effect and at the same time are efficient coolants. Even thick droplets of these liquids did not appreciably decrease the softening of germanium crystals by light.

Thus, there seems to be two energy ranges which cause softening of the surface layer of germanium crystals: one in the infrared with an energy range of 0.3–0.4 ev and another in the ultraviolet with energy higher than 3.0 ev.

The study of *p*-type germanium crystals was much less extensive. Two of these, containing 10^{14} and 10^{15} cm^{-3} concentration of ionized impurities, were tested. Their behavior was similar to that of *n*-type germanium crystals of the same purity. However, one *p*-type silicon crystal (purity unknown) exhibited much larger light softening (70%) than either *n* or *p*-type germanium [Fig. 1 (b)]. A few experiments conducted on *n*-type InSb and InAs (purity unknown) revealed that the hardness of their surfaces is also sensitive to light, but to a much smaller degree than that of germanium or silicon [Fig. 1 (c)].

The effect seems to be sensitive to the surface preparation, etchants, and the time and temperature of etching. However, not enough experiments were conducted to establish even a qualitative relationship between these variables. All germanium, InSb, and InAs samples in the experiment described above were etched with standard *CP*-4 solution, and the silicon crystals with a mixture of 75 HNO_3 and 25 HCl, by volume.

It is impossible at the present time to offer a detailed theory of this effect. The mechanism of the change of hardness with light must definitely be related to the energy states associated with dislocations. These, as has been pointed out at the beginning of this paper, are affected by the carrier distribution within the crystal. As the effect seems to be limited to a thin surface layer, which changes with impurity content (Figs. 2 and 3), it may be that this layer is identical with the space-charge layer[4] existing near the surface of semiconductors. Both infrared and ultraviolet light may alter the energy of dislocations in that layer and thus induce changes in its plastic properties, the former by changing carrier concentration within that layer and the latter by affecting surface electrons. However, on this basis, it is difficult to understand the similarity of the behavior of *p*- and *n*-type semiconductors. Another possible direction in which an explanation of this phenomenon should be sought would be to explore the effect of light on impurity atoms pinning down dislocations.[5] Such atoms could be ionized by light and become less effective in immobilizing dislocations. Again the effect of ultraviolet radiation would be difficult to fit into this scheme. It appears that more extensive experimental work is necessary before an adequate explanation can be advanced.

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

[5] Suggested by Dr. F. Seitz.

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Magnetic Analysis of the Uranium-Oxygen System*

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Magnetic susceptibility measurements have been carried out on the uranium-oxygen system in the composition range of UO_2 to $UO_{2.67}$. The existence of an antiferromagnetic transition at compositions close to stoichiometric UO_2 which had been previously reported by the authors has been confirmed. The data make it possible to define clearly the phase limits of the UO_2 and U_3O_8 structures and to determine unambiguously that the excess oxygen ions in the nonstoichiometric salts occupy interstitial positions in the lattice.

I. INTRODUCTION

Although UO_2 and U_3O_8 are stable stoichiometric chemical compounds, it is well known that as much as 75% oxygen may dissolve in uranium and in the process several phases may form at various concentrations of oxygen. While the crystal structures of the various phases appear to be known, it is not known just how the oxygen goes into the lattice and precisely at what compositions the new phases appear. Since these points are of some importance in the technology of the oxides of uranium, it is desirable to ascertain whether oxygen goes into the system interstitially or by causing uranium ion vacancies in an expanded lattice.

This investigation was undertaken with the intention of ascertaining by the techniques of magnetic analysis the following points:

1. Does the oxygen go into the lattice interstitially

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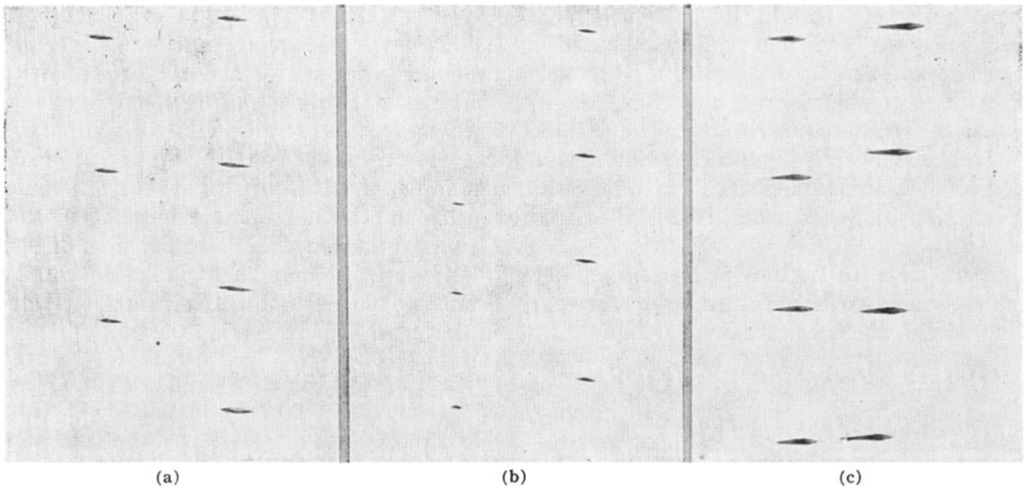

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