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¹Supplied by the Aluminum Company of America, Pittsburgh 19, Pennsylvania.

²J. W. McWane, J. E. Neighbor, and R. S. Newbower, *Rev. Sci. Instr.* **37**, 1602 (1966).

³M. Yaqub and J. F. Cochran, *Phys. Rev.* **137**, A1182 (1965). See also J. F. Cochran and M. Yaqub, *Phys. Rev.* **140**, A2174 (1965).

⁴We have obtained similar results using an altogether different measuring technique, the eddy-current method of C. P. Bean *et al.*, *J. Appl. Phys.* **30**, 1976 (1959). Though it is substantially less precise, this method has the advantage that no electrical contacts are attached to the specimen.

⁵Stringent requirements of magnetic shielding preclude a completely satisfactory study of the effects of external fields with the present apparatus (Ref. 2).

⁶It is plausible to attribute the T^2 term in gallium's

resistivity to electron-electron collisions, although this has been contested by M. Yaqub, D. Waldorf, R. Boughton, and W. A. Jeffers, Jr., *Phys. Letters* **23**, 423 (1966), on the basis of data concerning the resistance of thin plates. Such data are of limited relevance because, as emphasized by T. W. Moore, *Phys. Rev. Letters* **16**, 581 (1966), the effectiveness of normal phonon scattering is enhanced in thin plates by a factor of $(\Theta_D/T)^2$, where for gallium $\Theta_D \approx 300^\circ\text{K}$.

⁷G. J. van den Berg, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV, p. 194.

⁸The size-corrected resistivity ratio $\rho_{0^\circ\text{K}}/\rho_{273^\circ\text{K}} \approx 10^{-6}$ implies an impurity concentration on the order of 0.1 ppm.

⁹R. N. Gurzhi, *Zh. Eksperim. i Teor. Fiz.* **47**, 1415 (1964) [translation: *Soviet Phys.-JETP* **20**, 953 (1965)].

¹⁰G. T. Meaden, *Electrical Resistance of Metals* (Plenum Press, Inc., New York, 1965).

ACOUSTOELECTRIC CURRENT SATURATION IN TRIGONAL SELENIUM

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Acoustoelectric current saturation has been observed in single crystals of trigonal selenium. The hole drift mobility and its temperature dependence have been determined from this phenomenon. No evidence of a hopping mechanism is found.

Investigations of carrier transport in single crystals of trigonal selenium (often imprecisely classed as hexagonal) have led to strongly conflicting models of the mechanisms involved. Hall-effect¹ and thermoelectric-power² measurements show this material to be p type with an exponentially increasing mobility as the temperature is raised. From these experiments the hole mobility is found to be about $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at room temperature and less than $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 77°K . However, the mobility measured is strongly affected by illumination.² Two alternative mechanisms have been proposed to explain these observations. The first assumes that the hole transport occurs via a hopping process,³ rather than the normal band conduction, while the second involves the presence of potential barriers due to sample inhomogeneities.⁴ Phonon drag² and magnetoconductivity⁵ data, however, indicate that conduction occurs due to hole transport within the valence band and that the hole mobility is determined by interaction with lattice modes, as in the case of isomorphous telluri-

um.⁶ Considerably higher hole-mobility values of about $20 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 300°K are estimated from these measurements. Conventional transit-time measurements of drift mobility, used for monoclinic selenium,⁷ are impracticable because of the relatively high dark conductivity ($\sim 10^{-5}$ - $10^{-6} \Omega^{-1} \text{ cm}^{-1}$) at room temperature of presently available trigonal selenium.

The phenomenon of acoustoelectric current saturation,^{8,9} observable in piezoelectric semiconductors, can permit the measurement of drift mobilities. It has been demonstrated by Moore and Smith¹⁰ that the values obtained in CdS are quite consistent with those known for the majority carrier in this material. Acoustoelectric current saturation should occur in trigonal selenium since this allotrope of selenium is known to be strongly piezoelectric.¹¹ This Letter reports measurements of the temperature dependence of the hole drift mobility in single crystals of trigonal selenium made by the observation of this type of current saturation. The samples were prepared from good

single crystals recently grown in this laboratory by Keezer.¹² The growth of the crystals required the addition of ~ 100 ppm of thallium. Current saturation was observed and investigated for current flow perpendicular to the c axis (Y direction), and parallel to the c axis (Z direction). Evaporated nickel electrodes were used since they were found to make good Ohmic contact to the p -type selenium. Voltage pulses of variable duration from 5 to 50 μsec at a repetition rate of 30 pulses/sec were used to eliminate sample heating. Figure 1 shows typical current saturation observed at room temperature and 77°K. In the initial Ohmic region the current pulse shape was essentially congruent with that of the voltage pulse. As the saturation field was approached, however, the current initially rose to its extrapolated Ohmic value and then decayed to a final saturation value in about 50 μsec . This time

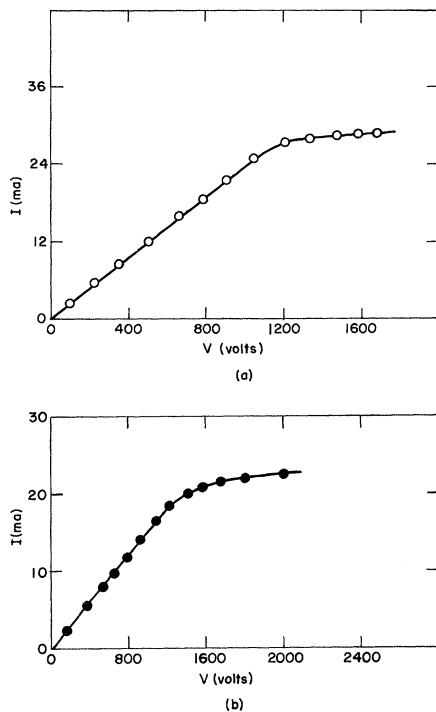


FIG. 1. Typical current-voltage curves for trigonal selenium. (a) Current flow along c axis at room temperature in sample 1.9 mm thick. Velocity of propagation of transverse mode down c axis $v_s = 1.76 \times 10^5$ cm/sec, used to evaluate drift mobility. (b) Current flow perpendicular to c axis (along Y direction) at 77°K in sample 1.8 mm thick. Velocity of propagation of transverse mode along Y direction (particle displacement in X direction) $v_s = 1.1 \times 10^5$ cm/sec, used to evaluate drift mobility.

constant could be reduced by illumination and the true saturated value thus observed within the voltage pulse duration. At the lower temperatures, illumination was essential since the dark conductivity was extremely low. Tests similar to those described by Smith⁸ were carried out and showed that the saturation was not a contact phenomenon. In addition, by etching the same sample to different thicknesses, it was established that the saturation field was not a function of sample thickness.

The observed saturation is therefore interpreted as being due to the interaction of the drifting holes with the piezoelectric lattice modes of the crystal. For fields such that the hole drift velocity would exceed the velocity of sound, the additional energy acquired by the holes from the field is passed on to these lattice modes and leads to their amplification. This mechanism is confirmed by the fact that buildup of acoustic noise was observed, as the critical field was reached and exceeded, using a transducer bonded to the sample. That this buildup was observed to saturate in a time essentially equal to the decay time of the current pulse is further evidence supporting this interpretation. The determination of the hole drift mobility along the Y direction can be readily made, since in this direction the carriers are expected to interact with transverse modes.¹³ Using the measured velocity for these modes,¹⁴ the drift mobility at room temperature along the Y direction is found to be $\cong 7$ $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$. For current flow along the Z direction, however, it is not clear which sound velocity to use because the carriers are not expected to interact with any mode in this direction.¹³ A similar situation exists for isomorphous tellurium but, since in this case the mobility is known from Hall-effect data, it appears that the velocity of the transverse mode propagating along the Z direction gives a consistent value for the drift mobility.¹³ It should be stressed, however, that the physical basis for this assignment is not understood at the present time. With this assumption, however, and using the measured velocity of this mode in trigonal selenium,¹⁴ a value of about 26 $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ is obtained for the hole drift mobility along the Z direction.¹⁵ This gives a mobility ratio of $\mu_{\parallel}/\mu_{\perp} \sim 3.7$, in good agreement with the conductivity ratio usually observed for trigonal selenium.⁴

Figure 2 shows the temperature dependence

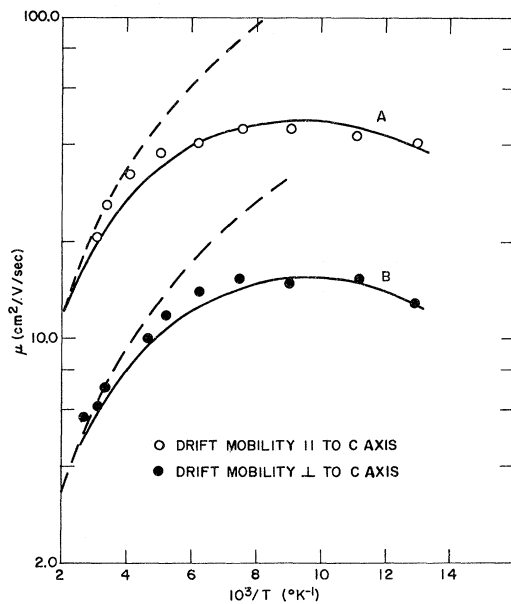


FIG. 2. Semilogarithmic plot of the drift mobility μ vs $10^3/T$. Both dashed curves show $\mu_L \propto T^{-3/2}$ with the curves normalized to the respective measured room-temperature values. Full curves A and B are the mobility variation expected from a combination of $\mu_L \propto T^{-3/2}$ with a mobility controlled by a density of hole traps of about $2 \times 10^{16}/\text{cc}$ lying 0.01 eV above the valence band.

of the hole drift mobility along and perpendicular to the c axis. The velocity of sound is expected to change by only a few percent between 300 and 77°K and this has been neglected. These data allow several interesting and significant conclusions to be made. Any hopping mechanism seems to be ruled out in the temperature range explored. The temperature dependence for both orientations is basically the same so that there appears to be no anisotropy in the transport mechanism. Both mobilities above about 250°K are determined by interactions with lattice vibrations since they decrease with increasing temperature in this range. However, it is difficult to specify the expected temperature dependence of the lattice mobility μ_L . Trigonal selenium has some characteristics which may require it to be more appropriately classed as a molecular crystal. Molecular crystals are in general characterized by narrow bands and low mobilities, and carrier transport under these conditions has been treated theoretically by Holstein.¹⁶ The predicted temperature dependence ranges between $\mu_L \propto T^{-1}$ and T^{-2} for limited temperature variations.

In Fig. 2 it appears that the experimental points at high temperatures are approaching a $T^{-3/2}$ curve. In view of Holstein's work, however, this does not necessarily imply that μ_L is determined by a conventional deformation-potential-type interaction. For temperatures below 250°K the measured drift mobility passes through a broad maximum. Assuming $\mu_L \propto T^{-3/2}$, the decrease of the drift mobility at low temperatures has two equally reasonable interpretations: either a trap-controlled mobility involving a density of hole traps of about $2 \times 10^{16}/\text{cc}$ lying 0.01 eV above the valence band, or charged-impurity scattering by a density of charged impurities of about $5 \times 10^{17}/\text{cc}$.

While a detailed interpretation of these data must await the results of further experiments, it has been possible to make significant conclusions regarding hole transport in trigonal selenium. Nevertheless, several important questions remain unanswered. In particular, a theoretical explanation of the current saturation observed along the Z direction is required. It is possible that the saturation in this direction may be due to "off-axis" modes, as suggested by Quentin and Thuillier for the case of tellurium.¹⁷

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SYMMETRY OF INTERFACE CHARGE DISTRIBUTION IN THERMALLY OXIDIZED SILICON

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It is well known that the surfaces of p -type silicon become inverted to n type upon thermal oxidation. The exact cause of this inversion is not well understood, but it seems to originate in positively charged defects located in the oxide near the oxide-silicon interface. One especially interesting aspect of this phenomenon is that the magnitude of the "built-in" interface charge depends upon the crystallographic orientation of the underlying silicon surface. The orientation dependence of the interface charge has been reported in the literature.¹⁻⁵ Of the limited number of orientations investigated, the (111) surfaces exhibit the highest density of charge and the (100) surfaces the least. Several questions immediately arise. What is the generalized dependence of the interface charge upon the crystallographic orientation of the underlying silicon? In particular, is there any other orientation that has still lower values of the interface charge density? In order to answer such questions it is desirable to obtain a more comprehensive orientation dependence of the interface charge. It is the purpose of this Letter to report the results of experiments in which the magnitude of this charge has been determined for all possible crystallographic orientations on one single-crystal specimen. This was accomplished by employing a hemispherical crystal of silicon on which the metal-oxide-semiconductor (MOS) capacitance could be measured for any desired crystallographic direction.

A single crystal of $6 \Omega \text{ cm}$, p -type silicon was ground and polished to form a perfect hemisphere of approximately 23 mm diameter. The equatorial plane was (111). The hemisphere was oxidized at 1200°C in dry oxygen to form a 1500-\AA -thick oxide and slowly cooled to room

temperature. The metallic-blue interference color was observed to be completely uniform over the entire hemisphere. The complete orientation was precisely determined by x-ray techniques on a Philips automatic single-crystal diffractometer (PAILRED).⁶ The crystal was then transferred to a goniometer specially constructed to carry out capacitance-voltage measurements on any desired orientation. The field-electrode contact could be made to any point on the oxidized hemispherical surface by means of a mercury drop.⁷ The contact to the silicon was made at the equatorial plane. Room-temperature capacitance was measured at 1 kHz and 100 Hz and the results used to obtain the interface charge as a function of the crystallographic orientation.

In the following discussion, Q^- represents the negative interface charge induced by the "built-in" positive charge located near the interface. The influence of work-function differences is omitted here and will be discussed later. For any given value of charge Q_g on the field electrode, the interface charge Q^- is given by

$$Q^- = Q_g + Q_{sc} + Q_t, \quad (1)$$

where Q_{sc} is the charge in the space-charge region of the semiconductor and Q_t is the charge trapped in the surface states at the oxide-silicon interface. The distinction between Q_t and the interface charge is that the former changes with the surface potential while the latter does not. Thus for any given point on the hemisphere, either side of Eq. (1) is a constant for all values of Q_g . In order to eliminate Q_t from Eq. (1), the interface charge was determined at the point where the surface potential is ze-