The comparison of (B6) with (B3) within the zero-point limit gives a critical density $n_e$, where the interelectronic process may intervene $n_e \sim 10^{14}$ cm$^{-3}$ for $\langle\epsilon\rangle \sim \epsilon_i$ [in fact, Eq. (B6) is deduced once the predominance of interelectronic process is assumed].


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# Changes in ac Conductivity of Silicon with Electron Irradiation at 0.5 K*

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Si was irradiated with 1.5-MeV electrons at 0.5 K. Changes in ac conductivity were dependent upon the dopant in the Si. No significant recovery of ac conductivity was observed with annealing up to 300 K. These results are consistent with previously published results at 1.6 K. These data support the suggestion that athermal migration of the Si interstitial occurs.

In a previous experiment[1] Si was irradiated at 5.0 and 1.6 K and changes in ac hopping conductivity were observed. This paper extends that work to 0.5 K.

A one-cycle pumped-He$^3$ cryostat was used in this experiment; the lowest temperature achieved was 0.3 K and the temperature during irradiation with $2\times10^{10}$ $e^-$/cm$^2$ sec was 0.5 K. A carbon resistance thermometer was calibrated for each run against the vapor pressure of He$^3$. The University of Illinois Van de Graaff accelerator was used to provide 1.5-MeV electrons. The Si samples were wafers lapped to 400-$\mu$m thickness and then etched to nominally 3 cm$\times$2 cm$\times$150 $\mu$m. Gold circles 0.64 cm in diameter were evaporated on both sides of the wafers opposite each other and the electron beam was collimated to 0.7 cm in diameter so that only the sample capacitor (the two evaporated gold plates with the Si dielectric between them) was irradiated. The sample was surrounded by a copper shield at 1.6 K (pumped He$^4$) with aluminum-foil windows for the beam. Electrical contact was made to the gold plates via evaporated gold wires which were misaligned with respect to each other on the wafers in order to avoid stray capacitance. The wafers were glued with GE 7031 varnish to

the $He^3$ cryostat. A General Radio 1620 capacitance bridge was used to measure the capacitance and dissipation factor of the sample capacitor in a three-terminal mode.

The dissipation factor of the sample capacitor is proportional to the ac conductivity of the silicon between the evaporated gold plates.[1] $\sigma_{ac}$ versus temperature is given in Fig. 1 for a typical sample. Above 12 K, free charge carriers dominate $\sigma_{ac}$; below 12 K, free carriers are frozen out and $\sigma_{ac}$ is determined by hopping conductivity and found experimentally[2] to depend upon the minority impurity concentration $N_{min}$:

$$\sigma_{ac} \propto \omega^{0.8} N_{min}^{0.85},$$

where $\omega$ is the measuring frequency. In Fig. 1, $\sigma_{ac}$ is seen to increase with irradiation; this increase will be referred to as $\Delta\sigma_{irr}$, which is a measure of the damage production.

There are two points of interest in Fig. 1. First, $\sigma_{ac}$ is seen to level off at low temperatures contrary to the theory of Pollack and Geballe.[2] Figure 2 illustrates this for several samples; $\sigma_{ac}$ even increases at very low temperatures for the 0.4-Ω cm material. This suggests the presence of a conduction mechanism in addition to hopping. Second, $\sigma_{ac}$ becomes increasingly irreproducible with decreasing temperature for a given sample as indicated by the error bars in Fig. 1. Measurements can be changed by (a) a single dc pulse, (b) momentary irradiation with electrons, (c) temperature cycling, or (d) noncumulative drift with time. Examples of dc-pulse effects are given in

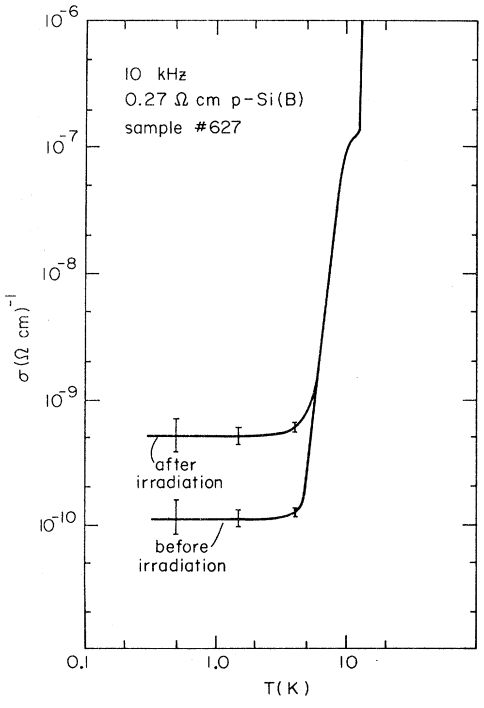


FIG. 1. $\sigma_{ac}$ at 10 kHz vs temperature for boron-doped 0.27-Ω cm $p$-type silicon.

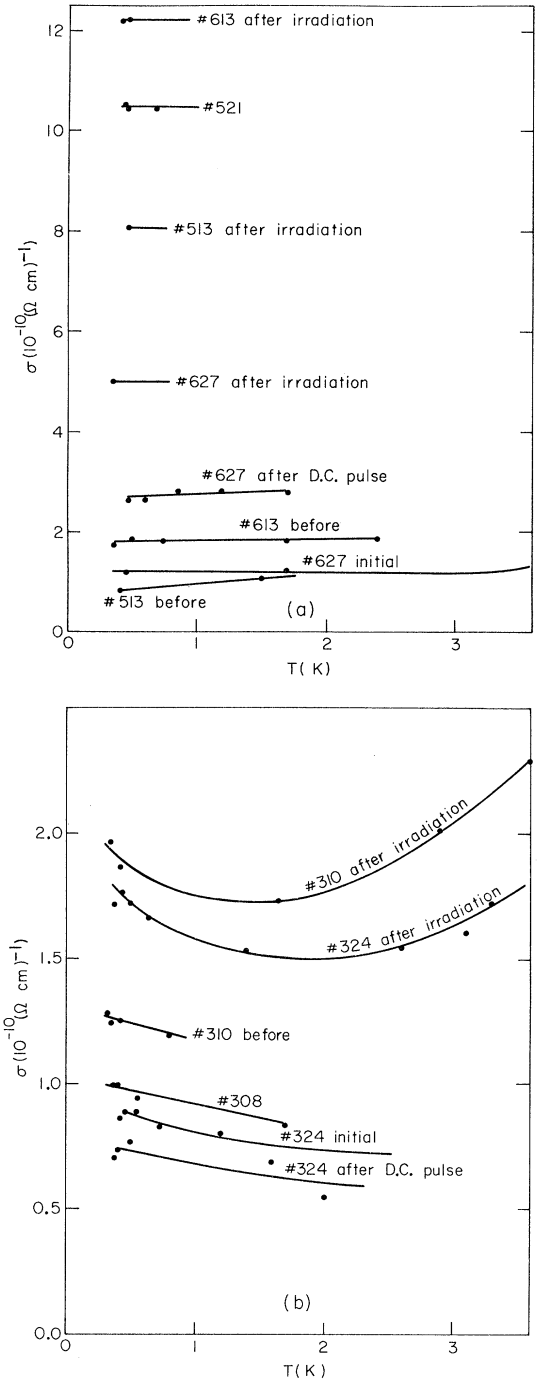


FIG. 2. $\sigma_{ac}$ at 10 kHz vs temperature for several silicon samples. (a) Boron-doped 0.27-Ω cm $p$ type and one phosphorus-doped (No. 521) 0.08-Ω cm $n$ type. (b) Aluminum-doped 0.4-Ω cm $p$ type.

Figs. 2(a) and 2(b). This may be an indication of failure to achieve complete thermal equilibrium of the distribution of charges between majority and minority centers.

In addition to the error bars for a particular sample indicated in Fig. 1, samples with the same room-temperature resistivity, prepared in the same way, were found (see Fig. 2) to differ by as much as a factor of 2 in $\sigma_{ac}$, in $\Delta\sigma_{irr}$, in the size of the error bars at low temperature, and in the leveled off $\sigma_{ac}$.

The $He^3$ cryostat used in this experiment had a cooling capacity sufficient to keep the sample at 0.5 K for a dose of $7-9\times10^{13}$ $e^-/cm^2$; the cryostat could be refilled with $He^3$ with the beam off. During a refill the sample temperature rose to 1.6 K (i.e., the temperature of the pumped-$He^4$ condenser). The data of Fig. 3 represent four irradiations separated by three such refills. Each refill is actually an anneal to 1.6 K for 10 min. $\Delta\sigma_{irr}$ was measured before and after each refill, but recovery greater than the accuracy of measurement was not observed. The range of measured values of $\Delta\sigma_{irr}$ is indicated in Fig. 3 by the pairs of points. The low-dose region of McKeighen and Koehler's[1] Fig. 10 is extrapolated to the very low doses of Fig. 3. For the 0.4-Ω cm material, the production rate is much lower and 18 irradiation-refill cycles were necessary to accumulate a significant $\Delta\sigma_{irr}$; only representative points are included in Fig. 4 for clarity. In this case, the experimental uncertainty in the measurement of $\sigma_{ac}$ is not much smaller than $\Delta\sigma_{irr}$, but comparison to McKeighen and Koehler's[1] Fig. 8 shows the production rates to be the same within the factor of 2 sample-to-sample variation. $n$-type material was also irradiated in this experiment, but no accumulated $\Delta\sigma_{irr}$ was observed due to the low doses available; this is consistent with McKeighen and Koehler's observation of a very low production rate in $n$-type Si for their much larger total doses of electrons.

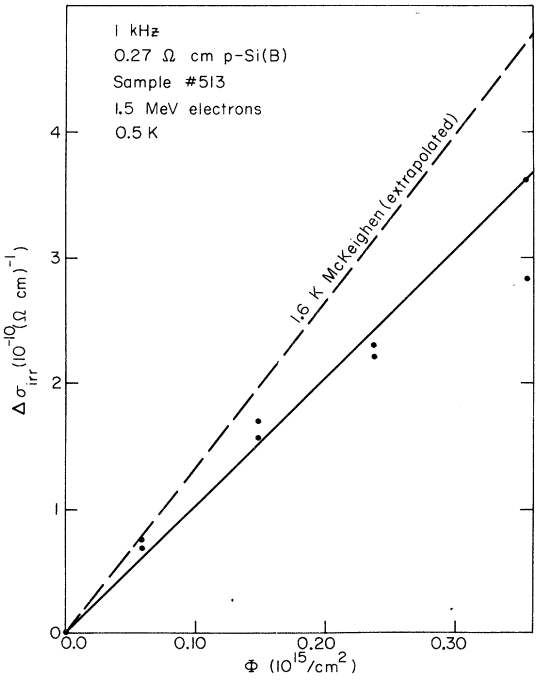


FIG. 3. $\Delta\sigma_{irr}$ at 1.0 kHz vs integrated electron flux for 0.27-Ω cm $p$-type silicon. 0.5-K data are compared to previously published 1.6-K data.

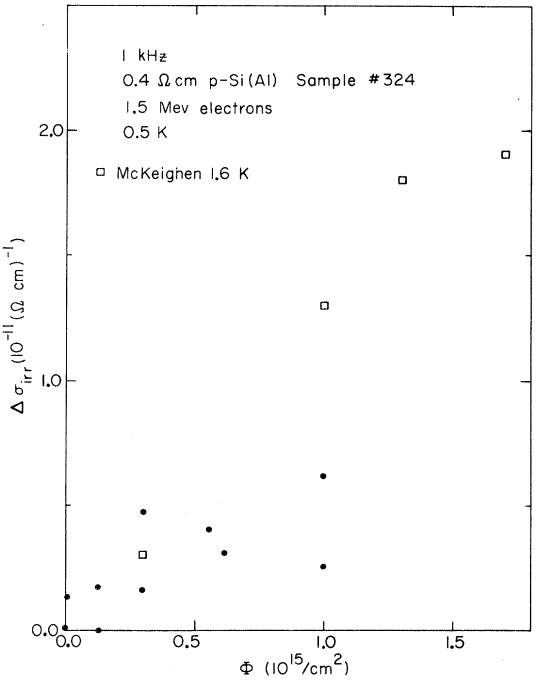


FIG. 4. $\Delta\sigma_{irr}$ at 1.0 kHz vs integrated electron flux for 0.4-Ω cm $p$-type silicon. 0.5-K data are compared to previously published 1.6-K data.

In summary, Figs. 3 and 4 show that the previous production rates $d\sigma/d\Phi$ (1.6-K irradiations with 4.2-K refills) and the present $d\sigma/d\Phi$ (0.5-K irradiations with 1.6-K refills) are the same within sample-to-sample variation for a particular doping concentration. No significant recovery has been observed in either experiment with annealing to 4.2, 78, and 300 K. For both temperatures,

$$\frac{d\sigma}{d\Phi}(0.27\ \Omega\,\mathrm{cm}) \cong 100\,\frac{d\sigma}{d\Phi}(0.40\ \Omega\ \mathrm{cm}).$$

The implication[1] of radiation damage which is impurity dependent and which does not recover with annealing is that the interstitials have already migrated—most to vacancies and some to impurity traps. This implication is contingent upon (a) the expectation[1] that interstitials and vacancies produce charged minority centers and (b) an ac-

conductivity model which predicts that the ac conductivity increases with the minority impurity concentration. It has been suggested[3] that interstitial migration at 1.6 K might best be understood by an athermal migration process; a model[4] for such a process has been proposed. The present extension of the migration temperature to 0.5 K adds further support to these suggestions.

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# Magnetic Susceptibility of Amorphous Semiconductors

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Previously observed paramagnetic contributions to the magnetic susceptibility of $As_2S_3$ and $As_2Se_3$ glasses are shown to be due to iron impurities. The density of singly occupied localized states is below $3\times10^{16}$ per $cm^3$ in ultrapure glasses. Careful measurements of the diamagnetic susceptibility of both the glassy and crystalline phases of several glass-forming semiconductors indicate that the difference in diamagnetism of the phases is small.

## I. INTRODUCTION

The magnetic susceptibility ($\chi$) of solids depends in general in a complicated way on the electronic structure, and the comparison of experimental results with theory is usually not straightforward. Nevertheless, studies of magnetic susceptibilities may provide a possible test on the correctness of some models of electronic structures. It is therefore of interest to investigate the magnetic susceptibility of amorphous semiconductors with the aim of obtaining some additional experimental information on a still unresolved problem of the electronic states in amorphous semiconductors. Busch and Vogt[1] observed a difference between the magnetic susceptibilities of amorphous and crystalline Se. At the melting point, $\chi$ of the crystalline form changed discontinuously in contrast to that of the amorphous form. Cervinka *et al.*[2] and Matyáš[3] found that $\chi$ of $CdGe_xAs_2$ and related glasses can be separated into a temperature-independent diamagnetic term $\chi_d$ and a Curie term $\chi_C$, which has been ascribed to unsatisfied Ge bonds. The paramagnetic contribution may under favorable conditions be observable also in electron spin resonance (ESR), and indeed, Brodsky and Title[4] observed ESR in nonannealed amorphous Ge, Se, and SiC films. The signal corresponded to spin concentrations of the order $10^{20}$ $cm^{-3}$. These free spins were associated with the dangling bonds at the inner surfaces of voids, and this assignment was later justified by some more observations.

Amorphous materials in which a paramagnetic term was observed are rather poor glass formers and must be produced by a fast quenching of the melt or by vapor deposition. Such materials are likely to contain a large concentration of unsatisfied bonds, and defects of this kind produce paramagnetic contributions to the susceptibility even in crystalline solids. Our aim was to study materials as close as possible to "ideal glasses," that is, glasses in which all chemical bonds are satisfied. We had therefore to choose good glass formers such as $As_2S_3$ and $As_2Se_3$, which can be produced in the amorphous forms even with relatively slow cooling rates.

The question which we asked was whether there are singly occupied states in the gap of an ideal glass, in other words, whether the mere loss of the long-range order produces singly occupied states in the gap. In the original Mott–CFO (Cohen, Fritzsche, and Ovshinsky) theory[5,6] of the states in the gap, the question of whether the states are doubly or singly occupied is not discussed. States