Quenched-In Recombination Centers in Silicon

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Measurements of lifetimes of minority carriers in *p*- and *n*-type silicon indicate that quenching from temperatures above 400°C introduces recombination centers. The energy of formation of these centers is about 0.6 ev. These centers anneal at temperatures in the neighborhood of the quenching temperatures with an activation energy for annealing of about 0.8 ev.

INTRODUCTION

LIFETIME of minority carriers in both *n*- and *p*-type silicon decreases considerably after it is heated to temperatures above 400°C and cooled rapidly. These changes are of a reversible nature in the range of temperatures between 400°C–600°C, for after short annealing cycles in the neighborhood of quenching temperature the lifetime is recovered. The present paper reports the results of experiments designed to obtain the activation energy for formation of recombination centers. The annealing of such centers has also been studied as a function of time and temperature. The results indicate that the quenched-in centers are generated within the crystal and may be imperfections such as vacancies or some unknown chemical impurities.

EXPERIMENTAL PROCEDURE

Silicon samples in the form of rods of dimensions 0.25 cm×0.25 cm×2.0 cm were cut from *p-n* grown junction single crystals. The junctions were located at the center of the rods, dividing them into approximately equal *n* and *p* parts. The rods were cleaned by etching them in CP-4, hot HNO_3, and rinsing in deionized water. The samples were heated on a tantalum tray in a Hoskins electric radiation furnace, which was lined with a Vitreosil fused quartz tube. The tube and the tray were cleaned in hot nitric acid and heated at 1300°C in nitrogen atmosphere for several hours. Quenching was accomplished in about 1 second by removing the samples from the furnace and dropping them into ethylene glycol. In the annealing cycle samples were cooled at a rate of 30°/minute from temperatures above 350°C.

The lifetimes were measured by the "junction recovery" technique previously described.[1] The ratio of resistivities on both sides of the junction was kept at least 100:1, so that lifetime on the high resistivity side was measured. Six crystals were employed in present experiments; their high resistivity sides varied between 2 and 25 ohm cm. Some of the crystals were rotated during growth,[2] and others were not rotated. Photoconductivity decay measurements[3] on single conductivity type crystals with resistivity up to 300 ohm cm have been made. The results showed that the behavior of these crystals on quenching and annealing was similar to those containing *p-n* junctions.

RESULTS

(a) Quenching Experiments

Samples of silicon have been heated to temperatures between 300°C and 600°C and quenched as described above. Their lifetimes were measured at room temperature before and after quenching. Typical results represented in a plot of the reciprocal of lifetime *vs* $1000/T$, where T is the temperature from which the crystals were quenched, appear in Fig. 1. According to the theory of Hall, Shockley, and Read,[4,5]

$$1/\tau \text{ is proportional to } N, \tag{1}$$

where τ is the lifetime and N is the density of recombination centers introduced in the present case on quenching. The plot indicates a relation of the form $1/\tau = Ce^{-E/kT}$. From the slope we obtain an activation energy E for formation of recombination centers of about 0.6 ev. These results have been shown to be independent of the following three factors: (1) length

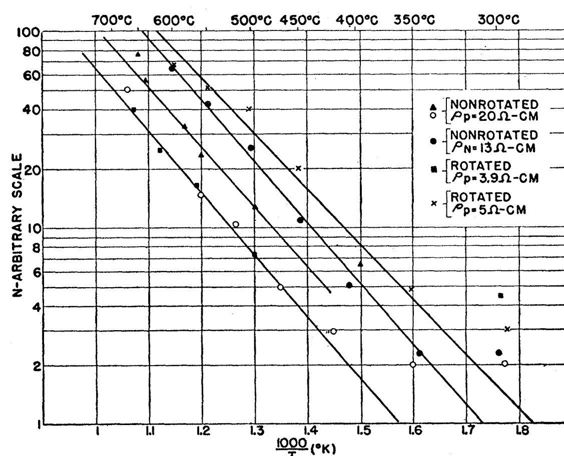

FIG. 1. Logarithm of $1/\tau$, the reciprocal of lifetime, *vs* $1000/T$. The slopes give activation energy for introduction of recombination centers.

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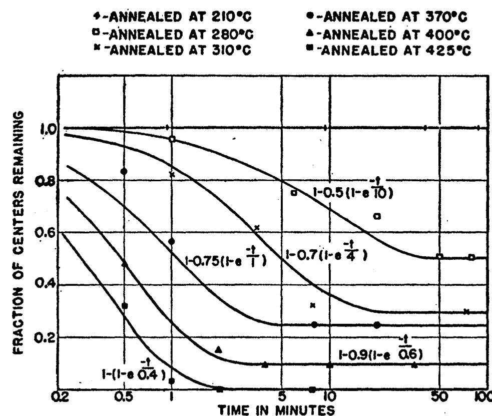

FIG. 2. Fraction of recombination centers remaining as a function of time and temperature of annealing.

of heating before quenching, which has been varied between 3 minutes and 5 hours; (2) prior history of the sample, i.e., a sample quenched from 550°C after being quenched from 500°C had the same lifetime as one quenched directly from 550°C (the converse is not true); (3) rotation or nonrotation during the growth of the crystals.

No changes in resistivity have been detected in the quenched nonrotated samples. The rotated ones showed resistivity changes as described by Fuller.[2] These changes which consisted of addition of 10^{14}–10^{15} donors/cm^3 were due to the heat treatment in the 300°–500°C range and were not due to quenching.

Hall effect studies were also made by H. Bridgers on samples in the form of bridges. Hall effect measurements as a function of temperature were taken before and after quenching. Within experimental accuracy no effect has been produced on quenching.

(b) Annealing Experiments

Results of annealing experiments on samples quenched from 450°C are shown in Fig. 2. We have plotted f, the fraction of recombination centers remaining as a function of temperature and the time of anneal.

The fraction is obtained from

$$f=\frac{N(t)-N_0}{N_Q-N_0}=\frac{\tau_Q[\tau_0-\tau(t)]}{\tau(t)(\tau_0-\tau_Q)}, \qquad (2)$$

where $N(t)$ is the density of recombination centers at time t, N_0 the density of centers before quenching, N_Q the density of recombination centers immediately after quenching, and τ the lifetime of electrons or holes—the subscripts having the same meaning as for N.

The significant features of annealing are: (1) At each annealing temperature there is a fractional anneal which takes place in the first few (up to 20) minutes, after which f reaches asymptotically a value characteristic of the annealing temperature. (2) Full annealing occurs only at approximately the same temperature from which the sample has been quenched. (3) By raising the temperature from T_1 to T_2 at any time during the annealing the fraction of annealed centers changes very rapidly from the curve corresponding to T_1 to one which corresponds to T_2.

Figure 2 shows that experimental points can be fairly well fitted by expressions of the form

$$f=1-[C(T)(1-e^{-t/p(T)})], \qquad (3)$$

where $p(T)$ is a time constant and $C(T)$ is the maximum fraction annealed. Figure 3 shows the dependence of p on annealing temperature. The semilogarithmic plot indicates an activation energy for the fraction annealed of approximately 0.8 ev.

DISCUSSION

We believe that the observed phenomena are related to some internal interactions rather than to diffusion from the surfaces. This is substantiated by experiments done on rods of large cross section which, after quenching, were etched to reduce considerably their cross section and did not show a difference in lifetime from outer surface to center. If diffusion from outside occurred, it had to proceed with a diffusion constant higher than 10^{-4} cm^2/sec at 450°C, which even though possible is unlikely.

Some possible internal processes can also be ruled out as hypotheses for the physical model involved. The possibility of impurities forming an atmosphere around dislocations which on heating and quenching can be dispersed and act as active recombination centers is not consistent with the fact that the fraction of centers annealed increases with temperature. If annealing occurred because the centers were attracted back to the dislocations, the temperature dependence would be opposite to that observed.

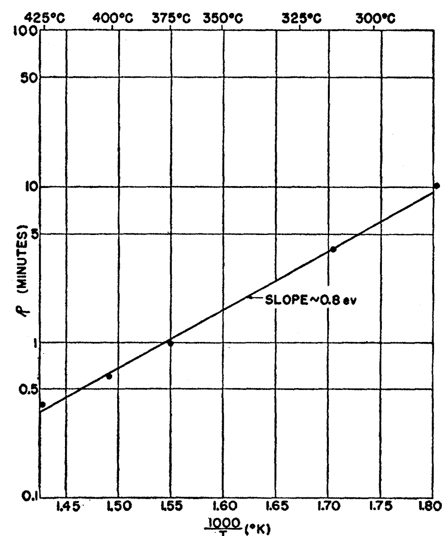

FIG. 3. Logarithm of time constant p as a function of $1000/T$. The slope gives an activation energy for annealing of 0.8 ev.

The results indicate that a simple thermally activated process cannot explain the observed changes. In particular, the fast increase in the number of centers which annealed at, e.g., 400°C after failing to anneal in 16 hours at 370°C requires an activation energy of about 5 ev. This activation energy is exceedingly high for a thermally activated process. It is interesting to add that the characteristics of the annealing are qualitatively similar to those observed by Logan[6] in germanium. One has to conclude that the process responsible for the observed changes is probably a complex one, possibly involving interactions between crystal imperfections of more than one kind.

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ACKNOWLEDGMENTS

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Thermal Conductivity of Germanium and Silicon at Low Temperatures

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Measurements are reported of the thermal conductivity, K, of high-purity n- and p-type germanium, and of a single crystal of n-type silicon at temperatures between 2 and 150°K. These confirm that in silicon and in annealed germanium the thermal conductivity is limited only by boundary scattering at temperatures below about $\theta/100$, where θ is the Debye characteristic temperature; while at temperatures above $\theta/10$, $K \propto T^{-n}$ where $n \simeq 1.3$ for germanium and $n \simeq 1.0$ for silicon. In the range of temperature just above the conductivity maximum, that is, from $\theta/20$ to $\theta/10$, no particularly rapid rate of change of K with T is observed, in contrast with the behavior found in pure dielectric crystals and bismuth. These features are discussed.

I. INTRODUCTION

RECENTLY, we reported[1] on the thermal conductivity of a high-purity single crystal of germanium, and since then further measurements on thermal conductivity and thermoelectric power have been made and some of the results published.[2,3] The thermal conductivity measurements, together with those just completed on an annealed specimen of germanium and a single crystal of silicon,[4] serve to emphasize some singular features of the thermal conductivity of these semiconductors.

Owing to the high electrical resistance of these elements, we should expect the heat to be carried almost wholly by the lattice waves and consequently the conductivity should exhibit the type of temperature dependence which is shown by crystalline dielectric solids (see, e.g., comprehensive reviews by Berman[5] and Klemens[6]). Previous work, particularly on germanium,[7-9,1] certainly suggests that lattice conduction is dominant, but even high-purity single crystals of germanium have not shown the marked rise in conductivity with decreasing temperature exhibited by such materials as diamond, sapphire, bismuth, or solid helium and ascribed to an exponential decrease in the thermal resistance due to phonon-phonon interaction at temperatures below $\theta/10$ (θ being the Debye characteristic temperature), where the probability of the so-called "umklapp-processes"[10,11,5] is decreasing rapidly as the temperature falls.

Thus it would appear that some fundamental reason exists for the behavior of germanium and silicon or that some physical impurity must be present which masks or obliterates an otherwise very high maximum in the conductivity at about $\theta/20$. In order to investigate the latter possibility, measurements were carried out on germanium specifically to determine the effect of annealing and on a single crystal of pure silicon.

2. EXPERIMENTAL

The specimens were mounted in a cryostat similar to that described previously[1] and the thermal conductivity

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