DEPENDENCE OF DEFECT INTRODUCTION ON TEMPERATURE AND RESISTIVITY AND SOME LONG-TERM ANNEALING EFFECTS

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I. INTRODUCTION

The effort reported here represents data which was obtained after the termination (June 1970) of our contractual investigation of lithium properties in bulk-silicon samples before and after irradiation. The objective of this phase of the study was to obtain the analytical information required to characterize the interactions of lithium with radiation-induced defects in silicon, and hopefully to develop a model of the damage and recovery mechanisms in irradiated-lithium-containing solar cells. The approach to the objectives was based on making measurements of the Hall coefficient and resistivity of samples irradiated by 1-MeV electrons. Experiments on bulk samples included Hall coefficient and resistivity measurements taken as a function of: (1) bombardment temperature, (2) resistivity, (3) fluence, (4) oxygen concentration, and (5) annealing time at temperatures from 300 to 373 K.

II. RESULTS

A. Carrier Removal

Previous work of several investigators (Refs. 1, 2) demonstrated that the defect introduction rate in phosphorus-containing silicon decreases as the bombardment temperature is decreased and also as the dopant concentration is increased at a fixed bombardment temperature. One of the objectives of our study was to determine the dependence of carrier-removal rate in irradiated silicon on bombardment temperature and lithium concentration. To achieve this objective, several Hall bars fabricated from 1500 Ω-cm and 5000 Ω-cm float-zone refined silicon and from 30 to 50 Ω-cm quartz-crucible silicon were diffused with lithium to concentrations from 2×10^{20} to 3×10^{23} Li/M^3 and irradiated at bombardment temperatures from 79 to 200 K. The rates of carrier-removal were determined after each bombardment. These rates measured in float zone (FZ) silicon after annealing to a temperature of 200 K versus the reciprocal of the bombardment temperature are shown in Fig. 1. Lithium concentrations of the samples used in the measurements are shown as a parameter. The carrier-removal rates were normalized at a bombardment temperature of 200 K, and the ordinate of the curves is labeled as the probability of defect formation. The curves shift along the temperature axis toward lower temperatures as the lithium density is decreased over three orders of magnitude. These concentrations of lithium correspond to resistivities from 0.03 to 20 Ω-cm. This shift of the temperature dependence portion of the curves is in qualitative agreement with the prediction of the interstitial-vacancy close-pair model (Refs. 1, 2) of radiation damage in silicon at low temperatures. It was previously reported (Ref. 3) that the saturated value of carrier-removal rate measured at a bombardment temperature of 200 K appeared to increase with lithium concentration. This conclusion is in agreement with the results obtained on the samples containing concentrations to 3×10^{23} Li/m^3.

A similar set of curves is shown in Fig. 2 for the samples fabricated from quartz-crucible silicon with lithium concentrations from 2×10^{21} to 3×10^{23} Li/m^3. The saturated value of carrier-removal rate obtained for the samples doped with 3×10^{23} Li/m^3 is equal to 10 m^{-1} which is the same value obtained for the samples doped with 2×10^{22} Li/m^3.

B. Annealing Properties-High Lithium Concentrations

Following the completion of the bombardments, the float-zone samples doped to 3×10^{23} Li/m^3 were annealed at temperatures ranging from 250 to 300 K. Hall and resistivity measurements were obtained on these samples as a function of time and measurement temperature. The time to half recovery, t_R of the mobility (T_M = 79 K) was determined from these annealing cycles, and the reciprocal of this quantity is shown in Fig. 3. The error in the measurement is large at the higher temperatures since the sample recovered to its original value of mobility in less than a minute at 300 K. Nevertheless, the activation energy determined from the slope of the curve is 0.68 eV which is close to the activation energy (0.66 eV) for lithium diffusion in oxygen-lean silicon measured by Pell (Ref. 4) and also reported (Ref. 5) in measurements made on solar cells.

C. Long-Term Annealing Effects

Results reported (Ref. 6) on the long-term annealing effects in lithium-containing quartz-crucible and float-zone samples with low lithium concentrations showed a disturbing property, namely, the continuous loss of carrier density (measured at low and high temperature) as a function of time in irradiated samples annealing at room temperature. These samples were recently remeasured, and the carrier densities measured as a function of time are shown in Fig. 4 for three samples. Two float-zone samples were doped to a low and a high concentration, respectively, and the quartz-crucible sample contained a high concentration of lithium. It appears that the runaway loss of carriers has finally ceased to occur in the quartz-crucible (>2 yr) and low-lithium-density sample of float-zone silicon. Thus, the precipitation-like process which produces a charge-neutral defect complex and which was previously postulated (Ref. 6) as one of the annealing mechanisms appears to equilibrate. The behavior of the other sample of float-zone silicon is typical of the more heavily doped samples, namely, an initial dissociation of defects with an increase of carrier density, and then they reach equilibrium over the long-term period.

III. DISCUSSION OF RESULTS

The irradiation temperature dependence of the production rate of impurity complexes in silicon has been explained (Refs. 1, 2) by a model based on the formation of close-spaced interstitial-vacancy pairs by electron bombardment. This model yields a probability P_C, of vacancy liberation from the interstitial to form vacancy-impurity defects described by

$$P_C = \left\{ 1 + g \exp \left[\frac{E_F(n_0, T) - E_M}{KT} \right] \right\}^{-1} \cdots \qquad (1)$$

where g is the ratio of the number of ways the state can be occupied to the number of ways the state can be unoccupied, $E_F(n_0, T)$ is the Fermi level for electrons which is a function of initial carrier concentration n_0 and temperature T, and E_M is the energy level of the metastable interstitial-vacancy pair. Equation (1) was used in an attempt to fit the data of Figs. 1 and 2. The preliminary results indicate that there is not a unique pair of values for the parameters g and E_M which will satisfactorily fit the data obtained on the float-zone samples over the three orders of magnitude range in lithium concentration. The best value of E_M appears to be $\approx$0.09 eV, but several values of g are required to fit the entire range of concentrations. In addition, the values of g are small (as low as 10^{-3}) and thus not physically reasonable. This model does not appear to be the complete description of defect production mechanisms in lithium-doped float-zone silicon over this range of concentrations.

The attempts at curve fitting were more successful with the quartz crucible samples. In this case, E_M = 0.07 eV and g = 0.1 gave a reasonable fit over the two orders of magnitude in lithium concentration of these samples. This higher value of g is more physically reasonable, and the lower value of E_M is in agreement with the value used by previous investigators (Ref. 1) in fitting their data on phosphorus-doped silicon. Our investigations have shown (Ref. 4) that the oxygen-vacancy defect is the dominating carrier-removal center in the lithium-containing silicon. Thus, it is reasonable to expect that these samples would behave similarly to the phosphorous-doped (5×10^{20} P/M^3, ρ = 10 Ω-cm) quartz-crucible silicon as our data indicates.

The mobility recovery shown in Fig. 3 demonstrated again in agreement with the detailed measurements obtained on solar cells (Ref. 5) that the diffusion of free lithium is definitely related to the recovery process. This conclusion applies to the short-term recovery period that is within the first few minutes or hours following bombardment.

The long-term annealing effects shown in Fig. 4 are important, since they indicated that the carrier density changes will finally equilibrate in lightly doped float-zone silicon or in the more heavily doped quartz-crucible silicon after a sufficiently long annealing time. This behavior is observed only under the conditions of these irradiations, namely the damage level was not large compared to the lithium concentrations. The author and other investigators (Ref. 7) have observed that after large fluences, the loss of carriers does not equilibrate, and the samples will return to the starting resistivity of the silicon before diffusion with lithium. This applies to both float-zone and quartz-crucible silicon.

IV. CONCLUSIONS

The simple close-pair vacancy-interstitial model does not completely describe the dependence of defect introduction on temperature and resistivity in lithium containing float-zone silicon. Better agreement of the model with experimental results is obtained in samples of lithium-containing quartz-crucible silicon. Further evidence of the relationship between diffusion of free lithium and recovery of damage was obtained. This was deduced from the activation energy for recovery of 0.68 eV measured in lithium-containing float-zone silicon.

Equilibrium and stability of the carrier density is possible after long-term annealing at 300 K in irradiated quartz-crucible (≳2 yr) or lightly doped (2 to 5 × 10^{20} Li/m^3) float-zone silicon (≲1 yr).

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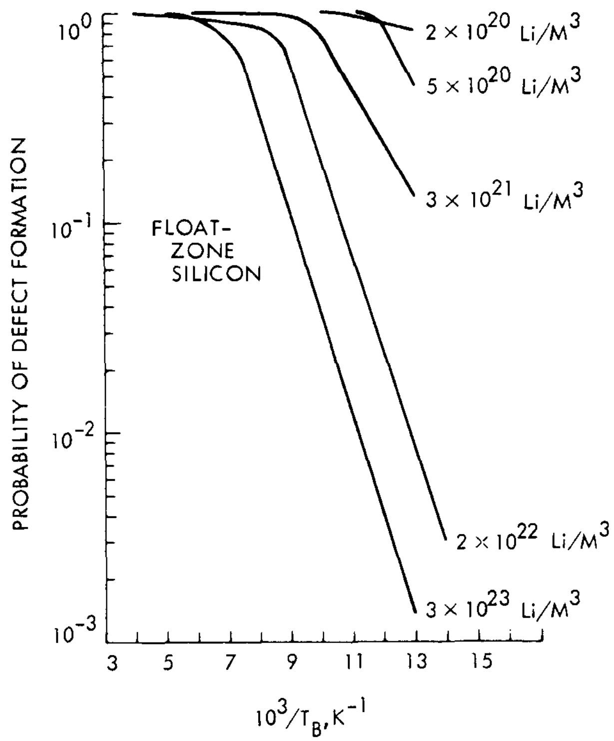

Fig. 1. Probability of defect formation versus reciprocal bombardment temperature for electron irradiated float-zone silicon measured at 79 K after annealing to 200 K. Initial lithium concentration is the curve parameter

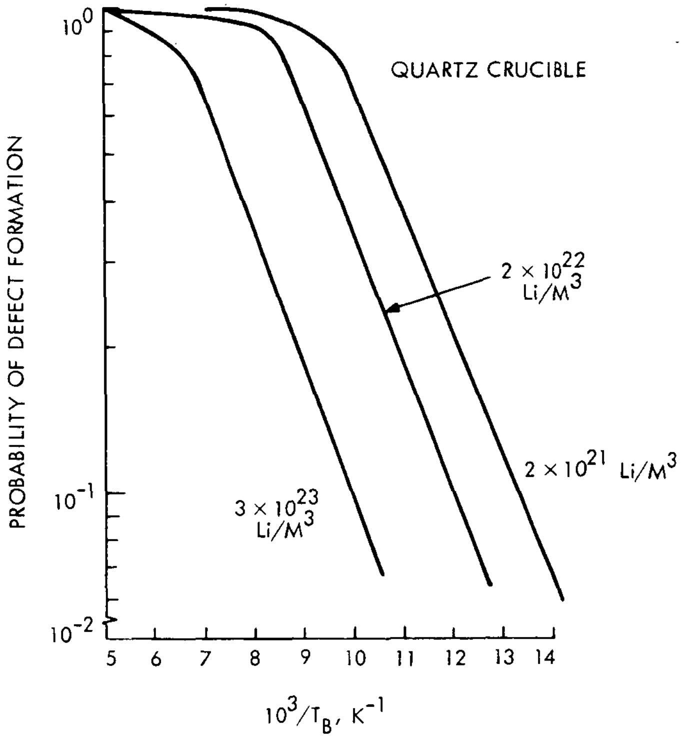

Fig. 2. Probability of defect formation versus reciprocal bombardment temperature for electron irradiated quartz-crucible silicon, measured at 79 K after annealing at 200 K. Initial lithium concentration is the curve parameter

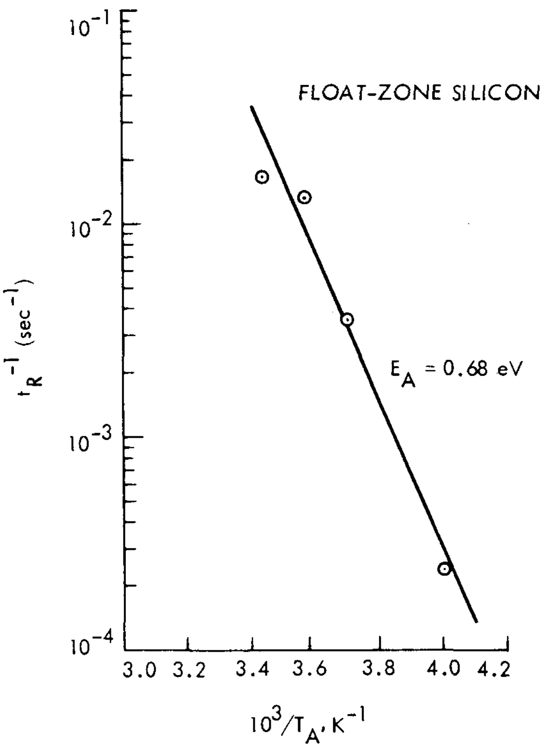

Fig. 3. Reciprocal half recovery time of the mobility in electron irradiated float-zone silicon versus the reciprocal annealing temperature. Measurements of mobility at 79 K. Activation energy for the recovery process is indicated. Initial lithium concentration 3 × 10^{23} Li/M^3

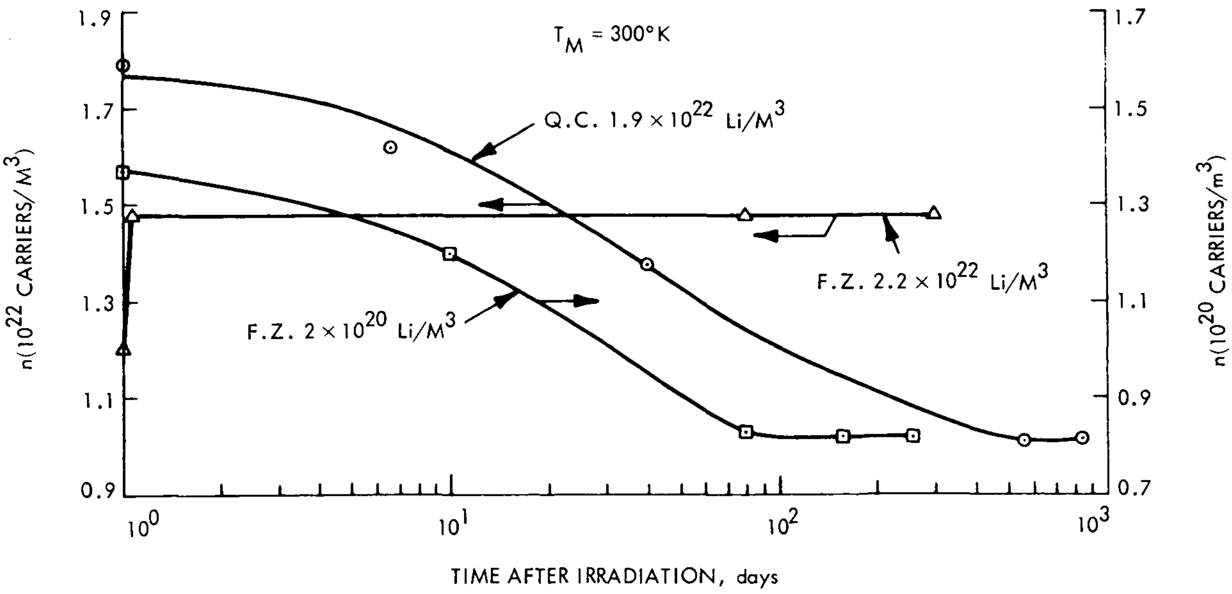

Fig. 4. Carrier density versus time after electron irradiation for samples of float-zone and quartz-crucible silicon, measured at 300 K. Initial lithium concentration is indicated for each sample