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Radiation Enhanced Diffusion in Silicon*

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Silicon samples, with a prediffused impurity layer, have been irradiated between 800°C and 1200°C, by energetic protons (250 kev to 1 Mev). After irradiation it is found that the impurity has diffused much faster than expected from thermal diffusion. This increase in diffusion coefficient takes place at some distance of the end point of the proton range, typically 2 to 5 microns. This result is consistent with a model of point defect diffusion, where defects (vacancies or aggregates) created by irradiation diffuse in the bulk of the sample. It is thus possible to measure diffusion coefficients of these defects. Activation energy for motion near 1.2 ev, jump frequency of 10^7 sec^{-1}, at 850°C, are obtained. These values could be attributed to a divacancy. The annihilation mechanism is investigated, and shown to depend on grown-in dislocation density.

Introduction

The effect of radiation induced point defects on the diffusion processes has been reported by a number of authors. It should, however, be pointed out that, in most of the experiments performed up to now, the diffusion enhancement occurs in a submicroscopic scale as, for example, in order—disorder transitions, where only a few lattice jumps are involved. We have been using the high sensitivity of semiconductor diffusion technology to show such effects on a larger scale—a few microns, involving thousands of interatomic distances.

Also, by using short range bombarding particles we have tried to separate the process of creation of defects from their effect on the diffusion of impurities, by allowing these defects to move an appreciable distance before being observed by diffusion enhancement. In this way, we expect to obtain data on the mobility of the defects themselves, and on their annihilation mechanism.

We assume that, near the end of their path, the protons used for irradiation create a large density of point defects which, if their mobility is large enough, are able to migrate to the surface or in the bulk of the sample. The local defect concentration will thus be increased and if these defects have some responsibility in the diffusion process—such as vacancies would have—the probability for a given impurity atom to make a jump will be increased, leading to an increased diffusion coefficient.

Experimental Procedure

We have reported the experimental technique in previous publications[1] and only a summary is given here.

The samples are thin slices (0.5×5×20mm) of single crystal silicon, *n* or *p*-type. A diffusion prior to the experiment, has created on the surface a layer, about 10 μ thick, enriched with an electrically active, substitutional impurity. Phosphorus, gallium, boron have been used. The diffusion is carried out in order to obtain a *p-n* junction.

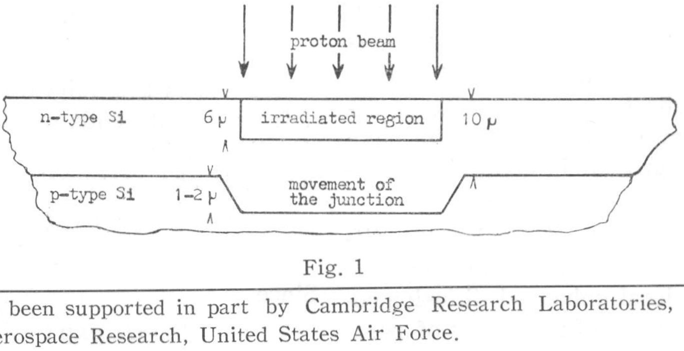

Fig. 1

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The doping level is kept low, in order to avoid lattice strains and formation of dislocations. The position of the junction, before and after irradiation, is revealed by a staining technique; it gives an isoconcentration contour.

The bombarding particles are protons, of 200 kev to 1 Mev (ranges in silicon from 3μ to 16μ), with an average beam current of $1\ \mu$ Amp on an area of $1\times5\text{mm}^2$. The defects are thus created a few microns from the *p–n* junction where their effects are observed.

During irradiation the sample is heated, between 600°C and 1200°C, so that the excess diffusion can take place during bombardment. However, a few experiments have been carried out where the sample was first irradiated at a lower temperature (*e.g.* 600°C) in order to store the defects, then heated at a higher temperature (1000°C) where the defects could move and act on the diffusion process of the impurity. This cycle, with storage and diffusion steps, was repeated a number of times in order to have cumulative effects.

It is mandatory that the sample be heated during irradiation, in order that the hydrogen atoms injected by the proton beam can diffuse out of the sample. Otherwise, bubble formation takes place which can even lead to sample breakage. However, such effects can be controlled and have been used for micromachining the sample prior to irradiation.

Results and Discussion

In a typical experiment (300 kev, $1\ \mu$A beam for one hour, irradiation temperature 1000°C) a movement of the junction as large as 3μ can be observed. The shape of the *p–n* junction, in this experiment, is strikingly similar to the 'collector dip' observed in double diffused *n–p–n* transistors. We think a similar explanation is possible in this case: the vacancy source would then be the emitter where a high donor concentration enhances the vacancy concentration. We have discussed such a process in a previous publication.[1)]

a) *Defect diffusion length*—Using the diffusion equation this measurement can be converted into a local enhanced diffusion coefficient. The influence of a number of parameters has been studied.

The distance between the defect source and the junction location can be varied, on a given sample. Such an experiment would give the free propagation length of defects, and, in case of a first order annihilation process, this would be a diffusion length. The experiments show indications of such process, with a diffusion length at 900°C of 1.4μ for samples with in-grown dislocation densities around $10^8\ \text{cm}^{-2}$, and 3.5μ for dislocation densities of 10^5-10^6cm^{-2}.

The first set of figures corresponds to one interatomic distance for the capture radius, which seems reasonable for annihilation on dislocations, while in the second case, the capture radius would be much larger, and this would imply another annihilation mechanism.

The average number of jumps for the defect before annihilation would be of the order of 10^9.

b) *Effect of temperature*— The effect of temperature shows a peculiar variation (Fig. 2).

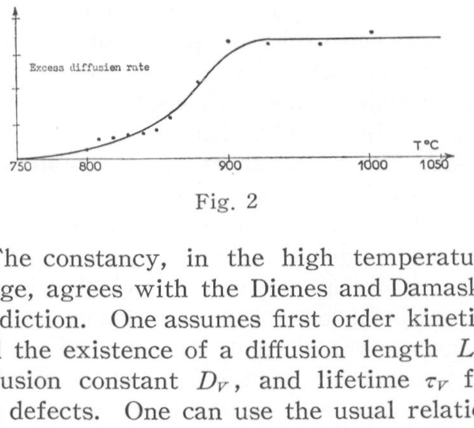

Fig. 2

The constancy, in the high temperature range, agrees with the Dienes and Damask[2)] prediction. One assumes first order kinetics and the existence of a diffusion length L_V, diffusion constant D_V, and lifetime τ_V for the defects. One can use the usual relation $L_V=\sqrt{D_V\tau_V}$. The excess diffusion coefficient D_i for the impurities is connected with the defect density n_V by:

$$D_i=Kn_V \exp(-E_m/kT) \tag{1}$$

where E_m is the migration energy for the defects. n_V depends on the creation rate g, the lifetime and the distance x from the source to the observation point, as

$$n_V=g\tau_V \exp(-x/L_V) \tag{2}$$

$$=gL_V^2 D_V^{-1} \exp(-x/L_V)\,. \tag{2'}$$

Since

$$D_V=D_0 \exp(-E_m/kT) \tag{3}$$

by comparing (1), (2′), and (3), one finds:

$$D_i = Kg/D_0L_V^2 \exp(-x/L_V) = KgD_0^{-1}L_V^2 \exp(-x/L_V)$$

and the temperature enters only through L_V.

In the low temperature range Eq. (2) breaks down, because the large rise in τ_V, from (3), would imply such high density of defects that radiation annealing takes place, limiting the density of defects. D_i would then fall as $\exp(-E_m/kT)$ with temperature. However, the steepness and shape of the experimental curve (Fig. 2) does not seem to correspond with the expected value of E_m for point defect. It should also be expected that the threshold temperature depends on the beam current, and this has been observed.

c) *Cycling experiments*—These two phase experiments are carried with the storage in the low temperature range—as defined above, while the diffusion phase is carried in the high temperature range above 900°C.

By varying the duration of both phases, one can observe for a constant integrated flux of irradiation and a given beam current, a saturation of the effect: when the storage time is longer than 400 sec. for the beam current used, no further diffusion occurs. This is interpreted as a lifetime for defects near 130 sec. at the edge of the plateau (850°C), with the assumption that the enhancement becomes independent on temperature when the lifetime is smaller than the accumulation time.

On the other hand, lowering the diffusion time down to 30 sec. has no apparent effect: this means that the lifetime at the highest temperature (1000°C) is smaller than 20 sec.

Conclusion

From the lifetime and the diffusion length values, one can obtain a detect jump frequency of the order of 10^7 sec^{-1} at 850°C. With a pre-exponential frequency factor of the order of 10^{13}, the migration energy E_m is 1.3 ev.

This migration energy, in view of the recent observations by Watkins[3] seems too large for single vacancies. It could correspond to divacancies.

However, other possible mechanisms could be invoked to explain radiation enhanced diffusion in this experiment. One possibility[4] could be the formation of dislocation loops which would act as diffusion short circuits. The evidence from the kinetics of the experiments seems to disprove such process: in the case of dislocation pipe diffusion, an after effect should be observed, the diffusion rate would depend on the induced dislocation density and the total diffusion time (time of irradiation + subsequent time at high temperature). No such effect is observed. This excess diffusion depends only, on the irradiation conditions (dose, temperature, and energy) and not on the thermal history of the sample. This shows, at least, that the defect involved in these experiments is a short lived one. The step in junction depth still exists after a post irradiation anneal of three hours at 1100°C*. Attempts have deen made for direct microscopic observation of these defects: the infrared and decoration technique did not show anything; X-ray topograph observations are under way[5].

References

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4 We are indebted to Dr. H. J. Queisser for this suggestion.

5 Authier and Lallemand: To appear in Comptes Rendus des Séances de l'Academie des Sciences, France.

DISCUSSION

Queisser, H. J.: I do not know what is plotted on your Fig. 2, since you give us numbers on the ordinate, however, it seems to indicate that you observe no diffusion enhancement below 750°C. In this connection it may be worth while to briefly report about some recent measurements done by Strack (Shockley Transistor). He

* This observation excludes the direct effect of acceptor centers due to radiation induced defects.

succeeded to dope Si in a glow discharge, using hydrogen and admixtures of PH_3 or B_2H_6. The bombardment with the hydrogen ions is thought to produce an excess of vacancies which give rise to a greatly enhanced diffusion of these dopants into the silicon. Such enhancement is observed even at temperatures well below 750°C, probably even below 500°C. Therefore a mechanism different from the one in your experiments seems to be operating.

Curien, H.: In our laboratory, Dr. Authier has investigated by x-ray microscopy the effects of the proton irradiation on the silicon samples of Dr. Pfister and Baruch. His results can be summarized as follows; 1). One does not observe any significant displacement of the dislocation lines. 2). External scratches present before irradiation are erased due to thermal diffusion on the surface (the specimens were annealed at 800°C). 3). The bulk deformation of the exposed region is revealed by a set of fringes.

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Vacancies in Germanium-Properties of Quenched-in Vacancies

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After the oxidation of surface to prevent Cu-contamination, intrinsic Ge with various dislocation densities were quenched from high temperatures to introduce vacancies (acceptors). The concentration of vacancies was $N_v=3.7\times10^{23}\exp(-1.9\,\mathrm{ev}/kT)$/c.c. The Cu-concentrations in the heat-treated samples were below 5×10^{13} Cu-atoms/c.c. Annealing curves of exponential decay type were observed for samples with large dislocation densities ($n_D\sim5\times10^3\sim10^5$). The activation energy for diffusion and diffusion coefficient were 1.2~1.3ev and $D_v=2\exp(-1.2\,\mathrm{ev}/kT)\mathrm{cm}^2/\mathrm{sec}$. For samples with small dislocation densities ($n_D\sim$less than 10^3), some of the annealing curves deviated from the exponential decay.

The cluster-formation of vacancies were estimated from these curves. The acceptor level of vacancy at 0.02~0.03 ev from the valence band was obtained from Hall and resistivity measurements with temperature range from 20°K to room temperature.

1. Introduction

Many works have been made to investigate the properties of vacancies in Ge by various methods. But their definite properties may be said undetermined. Production of vacancies can be classified into "direct production" and "indirect production." Quenching and radiation damage are direct productions. There may be many kinds of indirect productions. One of them is application of characteristic diffusion behaviours of Cu or Ni-atoms in Ge known as "dissociative diffusion[1]." By annealing of supersaturated Cu or Ni-atoms which are in substitutional sites to become acceptors[2], vacancies are left behind because the substitutional atoms jump to the interstitial sites and diffuse very rapidly to nuclei of precipitation. This principle was tried in Si by Woodbury and Ludwig[3]. Mayburg[4], Logan[5], Zhidkov[6] and others made quenching and annealing experiments to know the formation of defect and their diffusion properties. As for the temperature dependence, the quenched-in defect-concentration was reported by Mayburg[4] and Logan[5] as $3\times10^{23}\exp(-2.01\,\mathrm{ev}/kT)$/c.c. and $10^{22}\exp(-1.8\,\mathrm{ev}/kT)$/c.c. respectively. Tweet got higher value by different method—$4.5\times10^{22}\exp(-1.7\,\mathrm{ev}/kT)$/c.c.[7] and $4.5\times10^{22}\exp(-1.8\,\mathrm{ev}/kT)$/c.c.[8] Mayburg[4]