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The Observation of Damage Regions Produced by Neutron Irradiation in Lithium-Doped Silicon Solar Cells

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Regions of lattice disorder produced in lithium-doped float-zone melted n/p-type silicon solar cells by irradiation with mono-energetic neutrons at doses between 10^{10} and 10^{13}/cm^2 have been studied. The defect regions were revealed by chemically etching the surface of the solar cells and by observing carbon replicas in an electron microscope. It was found that the defect density increased with increasing irradiation dose and increased lithium content, whereas the average defect diameter was found to decrease. From thermal annealing experiments it was found that in the lithium-doped material the defect structure was stable at temperatures between 300 and 1200°K. This was found to be in contrast to the undoped material where at the lowest doses considerable annealing was observed to occur. The above results are discussed in terms of the theoretical predictions and models of defect clusters proposed by Gossick and Crawford and Cleland.

1. Introduction

It is now generally accepted that a localised cluster of lattice defects may be produced by a recoil from a single collision between an energetic neutron and an atom in the lattice [1-5]. Until recently, the behaviour of irradiated semiconductors has been interpreted on the basis of isolated Frenkel defects in terms of the models of James and Lark-Horovitz [6]. However, Gossick [7] and Crawford and Cleland [8] have proposed a model, more applicable to neutron-irradiated semiconductors, which predicts the existence of regions of highly localised damage. Their model suggests, for example, that in extrinsic p-type silicon the region of disorder may be considered to be intrinsic. Surrounding a disordered region is a potential well which arises because the position of the Fermi level relative to the energy bands is different within the disordered region compared to the outside. As a result a space-charge region or junction is created around the disturbed region, the diameter of which would depend upon the characteristics of the material being irradiated. The concentration of defects is considered to change abruptly at the boundary between the disturbed region and the undisturbed matrix. Such a combination of defects and space-charge regions would be regarded essentially as acting as insulators in an otherwise conducting medium.

Although electrical property measurements by Glosser [9] and Stein [10] have provided some support for the existence of damage regions such as those predicted by the above theories, to date very little work has been carried out to determine the exact structural nature of these regions. Fujita and Gonser [11] attempted to determine the size of the damage regions in irradiated germanium using an X-ray diffraction technique but were unsuccessful. More recently, there have been several attempts [12-14] to observe the damage regions in irradiated germaniums and silicon using the technique of transmission electron microscopy, however, an alternative and perhaps more successful method has been perfected by Bertolotti and co-workers [15-18]. This consists of irradiating a sample with fast neutrons, etching the surface with suitable chemicals and then obtaining a replica

for observation in the electron microscope.

The present work was undertaken to extend the earlier work of Bertolotti *et al* and specifically to attempt to determine the morphology of the damage regions, to study the effect of thermal annealing on these regions and the effects of lithium doping on them.

2. Experimental Technique

2.1. Material

The experimental work was carried out entirely on commercial lithium doped silicon solar cells obtained from Heliotek, a division of Textron Incorporated. The cells, 2 × 3 cm, were produced from float zone refined (oxygen free) single crystals of phosphorous-doped n-type silicon. The crystals were cut to give (110) slices into which boron was then diffused to produce a junction depth of 0.5 μm. Lithium was subsequently diffused into some of the cells using the "paint on" technique, to produce concentrations of 10^{15}, 10^{16} and 10^{17} lithium atoms/cm^3.

2.2. Neutron Irradiation

Samples of the undoped and lithium doped cells were irradiated with neutrons produced by a Crockroft-Walton generator, to doses of approximately 10^{10}, 10^{11}, 10^{12} and 10^{13} neutrons/cm^2. The neutrons were produced by bombarding a tritium target with deuterium. This source is highly mono-energetic and produces neutrons with energies of 14.7 MeV. The samples were irradiated at room temperature, the dose being controlled by varying the distance of the sample from the target. The relative dose received by each sample was measured by placing a thin copper foil of known weight behind each of the cells and after irradiation monitoring the decay of the Cu^{62} isotope, which has a half-life of 9.9 min.

2.3. Sample Preparation for Surface Replication

After irradiation the cells were sectioned by means of a diamond saw to produce samples approximately 4 mm long by 2 mm wide by 0.5 mm thick. The surfaces of the samples were then prepared for replication by mechanical grinding to a thickness of about 0.35 mm. The work damage produced by the mechanical processing was then removed by chemical polishing to a thickness of about 0.15 mm in a solution of nine parts nitric acid and one part hydrofluoric acid. During the polishing the sample was continually agitated to prevent the formation of gas bubbles at the surface. The polished surface was then etched for 6 sec with CP4A etchant (15 cc acetic acid, 25 cc nitric acid, and 15 cc hydrofluoric acid). A replica was made of the surface by evaporating a thin layer of carbon on to it. To provide mechanical strength to the replica a layer of chromium was deposited on top of the carbon. The replica was removed from the surface by means of mylar tape which was subsequently dissolved away in acetone. The replica was then observed in the electron microscope at accelerating voltages between 50 and 75 kV.

2.4. Thermal Annealing Experiments

In order to study the recovery of the neutron irradiation induced defect structures, samples were annealed at temperatures of 293, 593, 700, 900 and 1200°K. The samples were held at temperature in a glass vacuum furnace for a period of 10 min. After the annealing treatment the samples were prepared for replication and examination in the electron microscope as described previously.

3. Results and Discussion

Replicas taken from the etched surface of the unirradiated sample which contained no lithium were observed in the electron microscope and found to have a finely etched uniform structure which was devoid of any secondary features. In contrast, as can be seen from fig. 1, a similar sample after irradiation with 10^{12} neutrons/cm^2

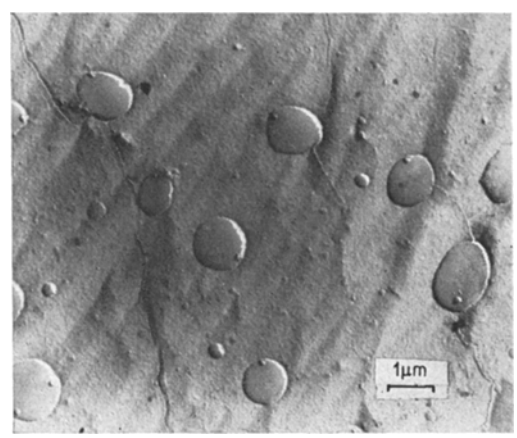

Figure 1 Typical surface replica of a solar cell irradiated to a dose of 10^{11} neutrons/cm^2.

shows a well developed secondary structure which takes the form of either circular or elliptical depressions (craters). This structure is typical of the appearance of etched surfaces of all of the samples, which contained no lithium, after irradiation. This structure appears to be similar to that reported by Bertolotti *et al* [17] and the average crater diameter of about 3000 Å at an irradiation dose of 10^{13} neutrons/cm^2 agrees very well with that of 2500 to 3000 Å measured by Bertolotti under identical irradiation conditions. It can also be seen from fig. 1 that many of the craters contain a second smaller depression of about 50 Å in diameter. According to Bertolotti the small depression corresponds to the position of the defect cluster caused by the irradiation damage and the larger crater corresponds to the space-charge region which surrounds the cluster. The dimensions of both of these regions are in fairly good agreement with theoretical estimates of between 2500 and 3000 Å, for the space charge region and 30 to 60 Å for the defect cluster, for the purity of silicon used in the present work irradiated to a dose of 10^{13} neutrons/cm^2, from the models of Gossick [7] and Crawford and Cleland [8].

Hemment and Gunnersen [13] have attempted to observe defect clusters directly by transmission electron microscopy in n-type silicon which was irradiated to a dose of 10^{19} *nvt* fast neutrons at a temperature of 60°C but they were unsuccessful. More recently, however, Pankratz *et al* [14] have observed defects in silicon irradiated at doses between 6×10^{17} and 5×19 nvt fast neutrons at a temperature of 125°C. Their material was of a lower purity than that of Hemment and Gunnersen having a resistivity of 300 Ω cm as compared to 1300 Ω cm. They reported a mean defect cluster diameter of about 22 Å in the as-irradiated material and also found that the defect density was proportional to the irradiation dose.

Magee and Morriss [19] have also reported observing defect clusters by transmission electron microscopy in neutron irradiated n-type silicon. Their specimens were irradiated to a dose of 10^{19} *nvt* fast neutrons at a temperature of 250°C. They report observing defect clusters of about 22 Å in diameter which agrees well with the defect diameter, reported by Pankratz *et al* [14]. However, Magee and Morriss also observed some larger defects with diameters above 100 Å which they concluded were related to closely spaced or overlapping individual small clusters.

It is not possible at the present time to make a more direct comparison between the size of the defect clusters observed by transmission electron microscopy and those observed in the present work by the surface replication technique due to the fact that the starting materials properties and conditions of irradiation are somewhat different in each case. However, there appears to be good evidence that defect clusters are formed as a result of irradiating doped silicon with energetic neutrons. In the present experiments the individual neutrons had energies of 14.7 MeV which is considerably higher than the energies of the majority of neutrons produced in reactors ($\simeq$ 1 MeV), therefore, it does not seem to be unreasonable that somewhat larger defect clusters would be observed.

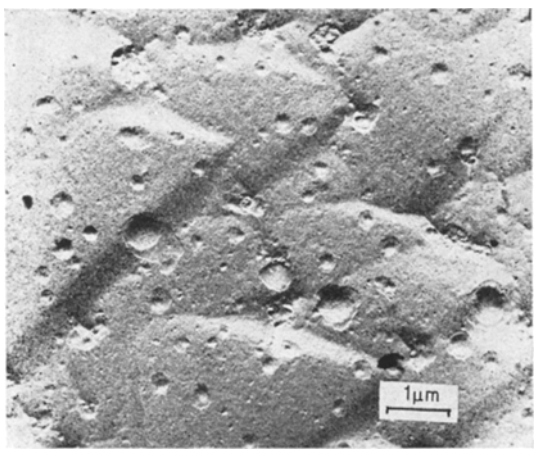

Figure 2 Typical surface replica of a solar cell doped with 10^{17} lithium atoms/cm^3 and irradiated to a dose of 10^{12} neutrons/cm^2.

Fig. 2 shows a typical micrograph obtained from a replica of a cell which was doped with 10^{17} lithium atoms/cm^3 and then irradiated to a dose of 10^{12} neutrons/cm^2. Here, the surface preparation was the same as that for the undoped material, however, the etching characteristics appear to be slightly different. The background structure is more irregular and although secondary structure in the form of craters is revealed the internal structure of the craters appears to be considerably pitted. The difference in the appearance of the craters in the doped and undoped material could possibly be due to the

presence of lithium precipitates which could modify the etching characteristics. The solubility limit of lithium in silicon is about 10^{15} atoms/cm^3 and some evidence for the presence of precipitated elemental lithium was obtained from transmission electron microscope observations of the unirradiated but lithium doped material. The structure was observed to contain many dark spots which were difficult to resolve as precipitates, however, selected area electron diffraction patterns were found to contain additional diffraction spots which could not be indexed with the diamond cubic structure of the matrix. They could, however, be indexed as body-centered-cubic and it was possible to estimate a value for the lattice parameter for this structure as 3.45 Å, which is in good agreement with that for elemental lithium.

The average diameter and density of the craters were measured as functions of the irradiation dose and amount of lithium dopant. These average values were obtained from measurements made upon six different areas, which were chosen at random for each of the replicated surfaces. Figs. 3 and 4 show, respectively, plots of the average defect density and diameter as functions of irradiation dose and lithium content. The range of actual values measured was approximately $\pm$ 15% about the average values plotted.

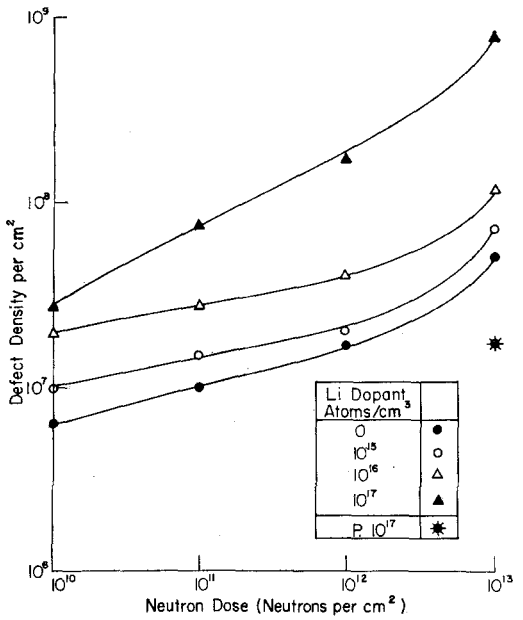

Figure 3 Average defect density as functions of irradiation dose and lithium dopant.

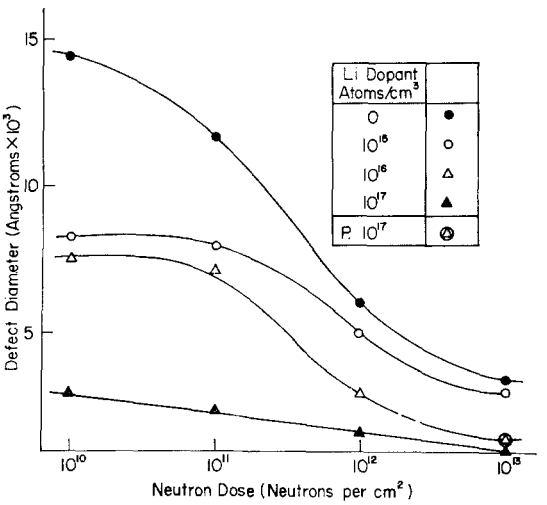

Figure 4 Average defect diameter as functions of irradiation dose and lithium dopant.

It was found that the defect density increased with both increasing lithium doping and irradiation dose. The defect diameter, however, was found to decrease with increasing dose and lithium content. For a given irradiation dose the total defect volume was found to remain essentially constant. The main effect of lithium appears, therefore, to be that it provides additional nucleation sites at which defect clusters can readily form under the present conditions of neutron irradiation at room temperature.

The average defect density and diameter was also measured for one solar cell produced from pulled silicon as the starting material which was doped with 10^{17} lithium atoms/cm^2. It was found, as can be seen in figs. 3 and 4, respectively, that at an irradiation dose of 10^{13} neutrons/cm^2, the density of defects observed in the pulled material is considerably lower than that observed in similarly doped float zone melted material. The average defect diameter, however, was found to be about the same. The main difference between pulled and float zone melted silicon is that the former contains oxygen as a significant interstitial impurity. It is possible that defects introduced into the pulled material by irradiation could readily become trapped by oxygen atoms thereby effectively reducing the number of defects available to form larger clusters, hence reducing the crater defect density. It would appear, therefore, that the ultimate size and distribution of the defect clusters is intimately related to the form and distribution

not only of the doping elements but also to the presence of other interstitial impurities.

The defect density and diameter was measured as a function of the thermal annealing temperature and these results are presented in figs. 5 and 6 respectively. It was observed that those samples which had been irradiated to a high dose or those which contained the largest amounts of lithium showed essentially no annealing either by way of changes in defect density or by changes in defect diameter. However, it was found that those samples which were undoped and irradiated at the lowest dose of 10^{10} neutrons/cm^2 showed considerable annealing at temperatures of 900 and 1200°K. This was reflected in both an increase in the defect density and in a decrease in defect diameter with an increase in annealing temperature. It appears from these results, therefore, that the defect structure which if formed during the irradiation at room temperature of either the doped or undoped material, at the higher doses, represents the most stable defect cluster size and density. Upon annealing, the large defect clusters found at the lowest irradiation dose in the undoped material appear to be unstable and collapse to form smaller defect clusters at a higher density.

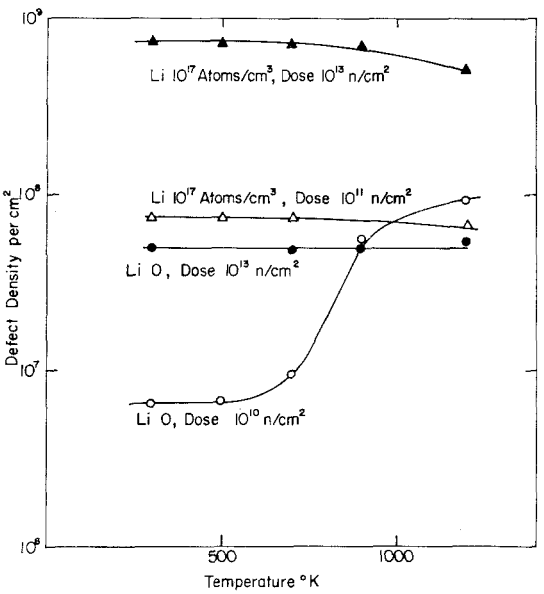

Figure 5 Effect of annealing temperature on the average defect density as functions of lithium dopant and irradiation dose.

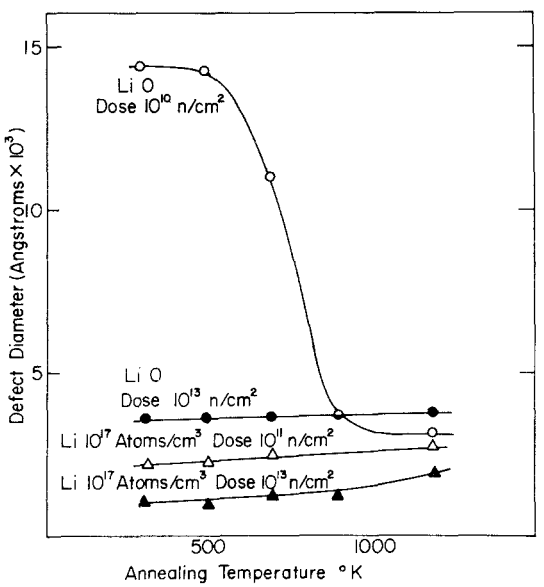

Figure 6 Effect of annealing temperature on the average defect diameter as functions of lithium dopant and irradiation dose.

The results of the annealing experiments carried out in the present work appear to be significantly different from those observed previously, from the recovery of electrical properties in neutron irradiated silicon by either Stein [20] or Passenheim and Naber [21]. Stein measured the effects of neutron damage at room temperature at doses up to 10^{10} neutrons/cm^2 on n-type float zone melted silicon ($\rho \simeq 6\ \Omega$ cm) by the degradation of minority carrier life-times. Upon annealing, recovery was found to occur over a broad temperature range from 330 to 500°K. Passenheim and Naber [21] carried out similar minority carrier life-time measurements on lithium doped silicon and found almost complete recovery at 380°K. It is again not possible to directly correlate the above results with the present work because of the wide differences in experimental conditions and starting material. However, it seems probable that the electrical property measurements are much more sensitive to more localised interactions between isolated neutron induced defects and interstitial impurities or doping atoms.

It is not clear from the present results what role lithium plays in the nucleation and stabilisation of the neutron irradiation induced defects. At the higher temperature used in the annealing experiments it is unlikely that lithium would remain in the bulk of the material. However, it is possible that at the irradiation temperature

the neutron induced defects are trapped at precipitated metallic lithium and form stable clusters. The subsequent annealing kinetics of the cluster, once it has reached stable configuration or critical size, could be independent of the presence of lithium. Hence the mobility of lithium in the lattice at the higher annealing temperatures would not necessarily influence the annealing kinetics of the defect clusters once they are formed.

The defect size and density observed in the undoped sample which was irradiated at the highest dose (10^{13} neutrons/cm^2) also appears to represent the most stable configuration for the defect clusters in this material. This is supported by the fact that the defect size and diameter, which is observed upon annealing the undoped material irradiated at a dose of 10^{10} neutrons/cm^2, tends to approach the values observed at the highest irradiation dose.

4. Summary and Conclusions

1. Evidence for the existence of defect clusters in neutron irradiated silicon solar cells was obtained by the technique of surface replication electron microscopy. The defects appeared as craters and ranged in size from 1500 to 15000 Å depending upon the irradiation dose and lithium dopant content. Under similar irradiation conditions, the defect craters were identical in both size and appearance to those described by Bertolotti *et al* [15-18] and were found to have characteristics similar to those predicted by the theory of Gossick [7]; i.e., the craters appear to be associated with the space charge region which surrounds a cluster of irradiation induced defects which are most probably lattice vacancies.
2. The crater defect density was found to increase with increasing lithium doping level, from about 6.5×10^6 defects/cm^2 for no lithium and a dose of 10^{10} neutrons/cm^2 to 7.8×10^8 defects/cm^2 for 10^{17} lithium atoms/cm^3 and a dose of 10^{13} neutrons/cm^2.
3. The average crater diameter was found to decrease with increasing irradiation dose and increasing lithium dopant, from about 15000 Å in the undoped material at a dose of 10^{10} neutrons/cm^2 to about 1500 Å for 10^{17} lithium atoms/cm^3 and a dose of 10^{13} neutrons/cm^2.
4. The total defect volume, for a given irradiation dose, appears to be essentially constant.
5. No annealing of the crater defect structures was observed in the temperature range 300 to 1200°K, with the exception of the undoped samples irradiated at doses of 10^{10} and 10^{11} neutrons/cm^2. In these latter cases it was found that the defect diameter decreased rapidly, and at the same time there was a significant increase in the defect density with increasing temperature.
6. There was some indication from selected area electron transmission microscopy that in the doped material lithium was present in the metallic form as a precipitate. It was suggested that the lithium precipitates may provide nucleation sites for the irradiation induced defects to cluster. However, it was thought that the lithium would play little part in the subsequent annealing of the defect clusters at the higher temperatures.

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