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RESEARCH STUDY OF STRUCTURAL DAMAGE PRODUCED IN SILICON SEMICONDUCTORS BY NEUTRON IRRADIATION

Semi-Annual Report

BY

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and Materials Science

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology (contract 952561), as sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

ABSTRACT

The main objectives of this program are to attempt to determine the size, distribution, morphology, and structural characteristics of the regions of lattice disorder which are produced by bombarding lithium doped silicon solar cells with neutrons. The effects of annealing the cells after irradiation are also to be studied.

The experimental work is being carried out entirely on the electron microscope using surface replication and thin film transmission techniques.

Suitable etching techniques for preparing the surfaces of the samples for the electron microscopy have been developed. It has been observed that in the as-received lithium doped cells, the lithium is present as a precipitate particle, thus more lithium may be present in the cells than as determined by the usual resistivity measurements.

Studies are continuing to investigate the effects of neutron irradiation.

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INTRODUCTION

It has been found in practice that when solar cells are exposed to the environment of space, they suffer severe degeneration due to defects caused by bombardment with a wide variety of nuclear particles.

The present work, which is supported by a NASA Contract Number NAS7-100, subcontracted by the Jet Propulsion Laboratories of the California Instititue of Technology, was undertaken to investigate the structural damage produced in lithium doped P/N silicon solar cells by neutron irradiation. From a detailed knowledge of the structural damage produced by irradiation it is hoped to be able to suggest treatments whereby the degenerative processes could be either reversed or prevented.

The main objectives of the present program are to attempt to determine the size, distribution, morphology and structural characteristics of the regions of lattice disorder which are produced in standard lithium doped P/N silicon solar cells after bombardment with neutrons having energies of about 14 MeV. The damaged regions are being studied as a function of irradiation dose, lithium doping level, and crystal orientation. Also the effects of annealing the samples after irradiation are being studied in order to determine whether or not there is any change in size, or distribution of the damaged regions with temperature.

The experimental work is being carried out entirely on the electron microscope. Two experimental techniques are being used; (1) surface replication, and (2) thin-film transmission electron microscopy.

The existence of regions of highly localized damage in semiconductors after irradiation by fast particles (neutrons) was first predicted by Gossick (1) and Crawford and Cleland (2). Their model for the disordered regions suggested that in a n-type germanium, for example, p-n junctions would seriously affect the lifetime of the semiconductor. Subsequently, experimental measurements of electrical properties by Closser (3) and Stein (4) have provided direct evidence for the existence of these regions. In the above experiments

the decrease in electrical conductivity of silicon was used as a measure of the carrier removal as a result of neutron irradiation, and the carrier concentration was obtained from Hall coefficient measurements. Further electrical studies of n-type silicon by Stein (5) have shown that neutron irradiation at 76°K produces light-sensitive defects at a rate that is independent of the concentration of crystal impurities. It was concluded from these observations that the light-sensitive defects produced in n-type silicon by neutron irradiation were vacancy-liberating clusters. The neutron induced defects were thus regarded as regions of high resistivity which were surrounded by space-charge regions. Such cluster-space-charge regions could be considered as insulators in a conducting medium. The light sensitivity of the irradiated silicon is believed to result from minority carrier trapping within the cluster-space-charge regions, which effectively reduces the insulating volume.

More recently, Stein (6) has shown that the behavior of defects produced in p-type silicon by neutron irradiation at 76°K was independent of the method of crystal growth and found that there was an illumination dependence similar to that previously observed in irradiated n-type silicon. He again attributed this effect to the presence of defect clusters. He also found that annealing the samples produced several diffuse stages between 150 and 550°K with the largest stage between 150 and 240°K.

To date very little work has been carried out to determine the exact structural nature of the regions of lattice disorder created by irradiation. Fujita and Gonser (7) have attempted to determine the size of the damaged regions in irradiated germanium using an X-ray diffraction technique but this technique did not provide any information about the distribution or morphology of the defects present. More recently, however, there have been several attempts to observe the damaged regions in neutron irradiated germanium and silicon semiconductors more directly using electron microscopy.

The first direct observation of defect clusters was made by Parsons, Balluffi and Koehler (8) in thin germanium films using transmission electron microscopy. The number of regions which they observed was in good agreement with their theoretical estimates from electrical property measurements and a mean defect diameter of 53 Å was measured. Hemment and Gunnersen (9) have attempted to perform similar transmission electron microscope experiments on thin-film n-type silicon samples which were irradiated with fast neutrons with integrated doses ranging from 5×10^{16} to 10^{19} neutrons/cm^2 but they reported that none of the irradiated samples examined showed any evidence for the existence of defect clusters. However, more recently Pankratz, Sprague and Rudee (10) have been successful in observing defect clusters in neutron irradiation damaged silicon by transmission electron microscopy. They found that the mean defect image size dependent on the impurity content of the silicon and on the annealing treatment, ranging from a maximum of about 40 Å in the as irradiate material to about 22 Å in the annealed material. The defect density was found to be approximately proportional to neutron dose. An alternative method for observing defects in germanium and silicon semiconductors, which was tried unsuccessfully by Chang (11) and Noggle and Stiegler (12), and later perfected by Bertolotti and co-workers (13, 14, 15), consists of irradiating the semiconductor with fast mono-energetic neutrons, etching with suitable chemical etchants, then constructing a replica of the surface and finally observing the replica in the electron microscope. Bertolotti and his co-workers have irradiated silicon samples with a fluence of 6×10^{12} 14 MeV neutrons/cm^2 from a Van de Graaff accelerator. They found that on etching the surface of the irradiated samples craters were produced, the dimensions of which were found to compare with the dimensions of the space-charge region as calculated according to the theory of Gossick (1) and Crawford and Cleland (2). Within the craters a smaller well defined region

could also be identified which had a mean dimension of about 500 Å. This compares very favorably with the theoretical estimates of about 600 Å for the damage region in the crystal.

The above results, it was concluded, seem to agree with the picture of the creation of clusters of defects in silicon and with the existence of a junction between its damaged region and the silicon matrix, as was also found to be the case in germanium.

The work undertaken in the present contract research was designed to extend its earlier experimental observations and, specifically, to try to determine the true structural nature of the damaged regions and to study the effects of annealing these regions.

It was decided to use neutrons as the irradiating particles for the following reasons: (a) neutrons carry no charge, therefore the damage effects of charge are absent, leading to possible simpler interpretation of the data; (b) the momentum of the particle can be easily controlled by means of an available neutron source; (c) the momentum damage produced by neutrons should be directly comparable to that produced by protons of similar energies.

In the environment of the van Allen radiation belt or in deep space the entire spectrum of types and energies of radiation should be present. Certainly 10 MeV protons can be expected. These energetic particles should produce severe structural damage of the type already described and found experimentally by other workers. Consequently, the work undertaken here is designed to contribute to the understanding and possible solution of the problem of the damage caused to silicon solar cells by high momentum particles.

Progress

A thorough literature survey was initiated at the beginning of the contract period in order to review the previous work in the general area of irradiation damage effects in semiconductors. It was found that very little work had been done previously in the area of the present investigation and that some of the past results were in conflict. For example, some workers had observed defects by means of transmission electron microscopy or surface replication and others had not.

Three commercial manufacturers of silicon solar cells were contacted for quotations to produce a number of lithium doped cells at four doping levels. These were the Northrop Corporate Laboratories, Heliotek Division of Textron, and Centra Laboratories. Heliotek offered to supply undoped samples at $20 each and doped samples at $35 each and quoted a delivery time of three months. An order was placed with Heliotek for six undoped cells and five cells each of doping level 10^{15}, 10^{16}, and 10^{17} atoms/cm^3. A partial shipment of the cells including five undoped and three cells doped to 10^{17} atoms/cm^3 were received within one month of placing the order, however, the remainder of the cells are still to be delivered. Due to the delay in receiving the total shipment of cells, progress in the present program has been considerably held back and so far, it has not been possible to have any cells irradiated.

From the review of the literature it appeared that the method of preparing the surface and etching the sample was very critical if any defects were to be observed either by thin film transmission or by surface replication electron microscopy. Therefore, because of the delay in receiving the total shipment of cells, it was decided that the time could be spent profitably in the present investigation to compare several different etching techniques and try to establish the optimum conditions.

Initially it was decided to concentrate on evaluating etchants suitable for polishing and etching the surface of the solar cells so that carbon replication

of the surface could be accomplished with good resolution. One of the undoped cells which was approximately 1 x 2 cm in dimensions was cut into smaller samples about 1 mm square and about 0.45 mm thick. Several etchants, which were known to have been used with silicon based materials, were tried. The chemical compositions of these etchants are given in Table I.

The CP-4A etchant (15) was found to have the best overall characteristics. For example, it gave a smooth unoxidized surface which was reproducible. The "Westinghouse silver etch" was also found to be satisfactory. It produced a good surface which etched satisfactorily in about 30 secs. A greyish oxide film was observed to form at the beginning, but it disappeared toward the end of the etching period. Under the electron microscope the carbon replicas taken from the surface etched with the above etchant showed good resolution. Both the "Dash" and the CP-4 etches polished fairly successfully but there was some tendency toward oxidation toward the end of the etching period. It was found, however, that this oxide could be removed by the addition of a few drops of bromine to the etchant in the later stages. The "sirtl" etch was the least successful, producing a poor surface with considerable oxidation. Figure 1 shows a typical micrograph of a replicated surface. The sample was etched with the CP-4A etchant and then the surface was shadowed with carbon. The carbon was further shadowed with chromium for mechanical strength and stability. It can be seen from the micrograph that the surface is relatively smooth with some slight pitting probably at imperfections.

As was mentioned in the introduction, there has been little use made of transmission electron microscopy to study defects in silicon, however, Booker and Sticker (17) have described a method of preparing silicon specimens for examination by transmission electron microscopy. They have made use of a jet electrolytic polishing technique which is similar to that of Riesz and Bjorling (18).

TABLE I. ETCHANTS FOR PREPARING THE SURFACE OF SILICON PRIOR TO REPLICATION

ETCHANT	COMPOSITION
1. "Sirtl"	1 part (33%) by weight aqueous solution CrO_3 and 2 parts HF.
2. "Dash"	3 parts HNO_3, 2 parts CH_3OOH, 1 part HF.
3. "CP-4"	2 parts HF, 1 part CH_3OOH, 1 part HNO_3.
4. "Westinghouse silver etch" (W-Ag)	40 cc (50%) HF, 20 cc HNO_3 40 cc H_2O. 2.0 g. silver nitrate dissolved in distilled water.
5. "CP-4A" (15)	15 cc Acetic Acid, 25 cc HNO_3 15 cc HF.

Fig. 1. Surface replica of undoped silicon solar cell
X 15,000

In order to prepare silicon samples so that they are sufficiently thin for examination by transmission electron microscopy silicon specimens less than approximately 10,000 Å are required. There are two main difficulties associated with the preparation of such specimens. First, a strictly nonpreferential thinning process is required. Second, owing to the extreme brittleness of semiconductor materials in general, the thinned specimens frequently break during handling before they can be examined in the electron microscope.

In the present investigation it was decided to follow the Booker and Stickler technique because very small samples could be processed which could be transferred directly to the specimen holder of the electron microscope without any further treatment. Therefore, a simple jet chemical polishing machine was constructed. A schematic diagram of the machine is shown in Figure 2. The solution which was selected for a rapid polishing rate with a high quality nonpreferential polish consisted of 9 parts HNO_3 (60 %) and 1 part HF (48%). Because of the corrosive nature of the polishing solution plastic materials were used throughout the construction of the machine. The chemical polishing solution is applied to the surface of the specimen through a plastic tube which terminated at the end by a vertical nozzle. Fibre optics are passed through the tube, supplying the polishing solution, to provide a light pipe by which the lower side of the specimen can be illuminated. The specimen holder has a hole of 1 mm radius on which the sample rests and it is held in place by means of a disc, with a concentric hole to that of the specimen holder, which is screwed down on to the specimen. Initially an alarm was used to signal the end point of the polishing. This was activated by means of a photoelectric cell which was sensitized by means of a light beam passing through the perforated specimen. It was found, however, that this technique was not very efficient because the alarm did not sound until the sample had a fairly large hole in it and this

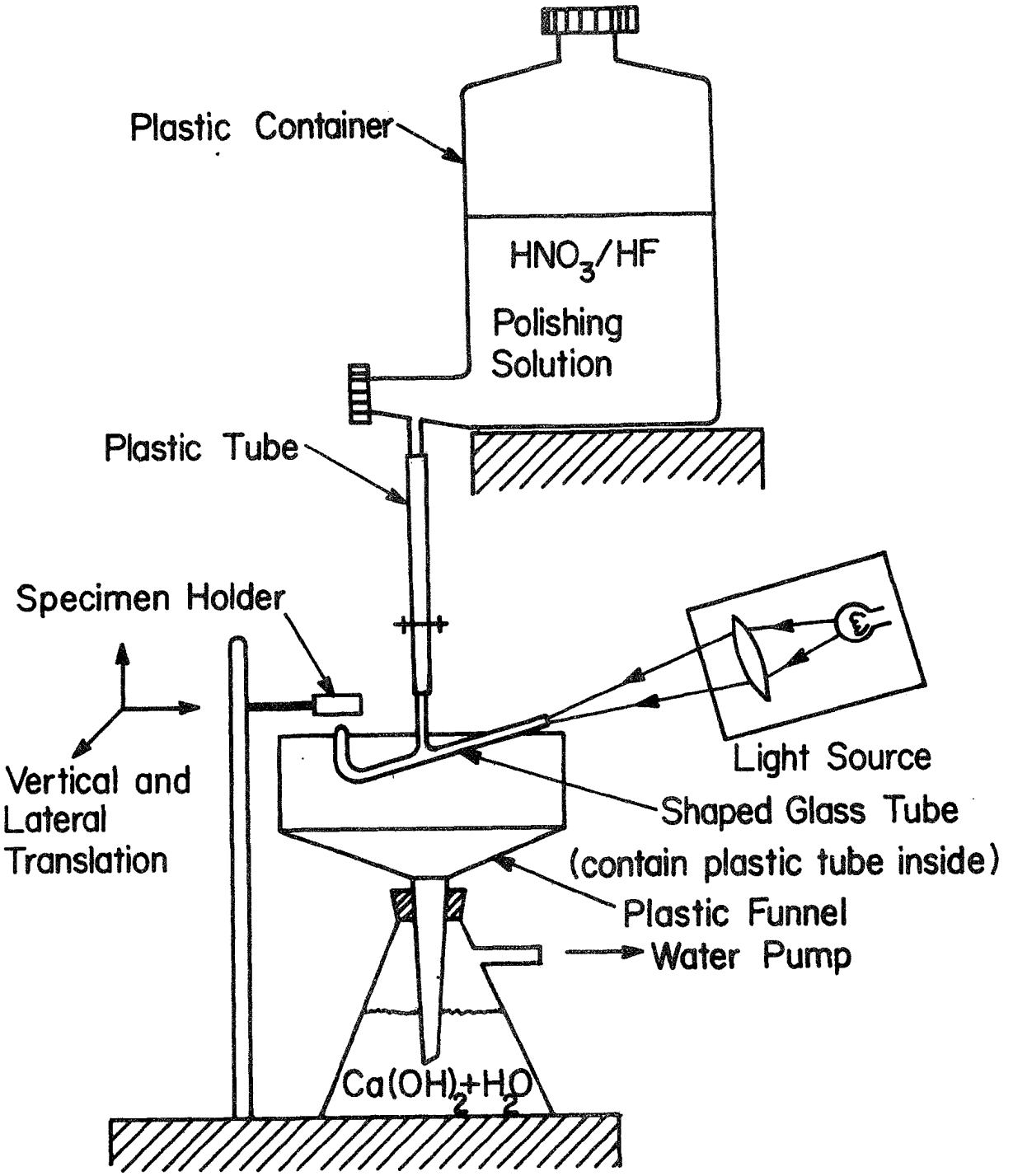

Fig. 2. Schematic diagram of chemical polishing machine.

condition was found to produce poor samples for observation in the electron microscope. Once the sample was completely perforated the polishing solution attack became very rapid at the edges of the hole and the thinned down section was rounded off leaving the material at the edges too thick to be penetrated by electrons in the microscope. The technique was modified, therefore, such that during the polishing the upper surface of the specimen could be observed by means of a binocular microscope. It was noticed that after a few minutes of polishing a small dark red spot appears due to light being transmitted through the thinnest-portion of the specimen. As polishing continues the spot changes to light red, orange and pale yellow and then a small hole appears. Polishing is usually terminated at the yellow stage when the thinnest portion of the specimen is then less than approximately 5000 Å thick. The specimen is rinsed with distilled water, acetone, then in ethyl alcohol and finally dried. A finer control of the end point was obtained by removing the specimen at the red stage and then dipping it in the the polishing solution and examining it at intervals by transmitted light. However, it was found in some instances that preferential etching did occur if the hand dipping was carried too far.

Experimental Results

Figure 1 and 3 show photographs taken from surface replicas of the etched surfaces of the undoped and lithium doped (10^{17} atom/cm^3) samples respectively. It can be seen that the undoped surface shows only a few irregularities in an otherwise reasonably flat surface. Although there were a few regions, as illustrated in Figure 1, which contained what appeared to be some form of inclusion, probably an oxide. In comparison, the surface of the doped sample, as shown in Figure 3, was found to be heavily pitted, producing an effect which is often observed in materials which contain a large number of precipitate particles.

The thin film transmission pictures also support the above observation. The transmission photograph of the undoped material, Figure 4, shows a

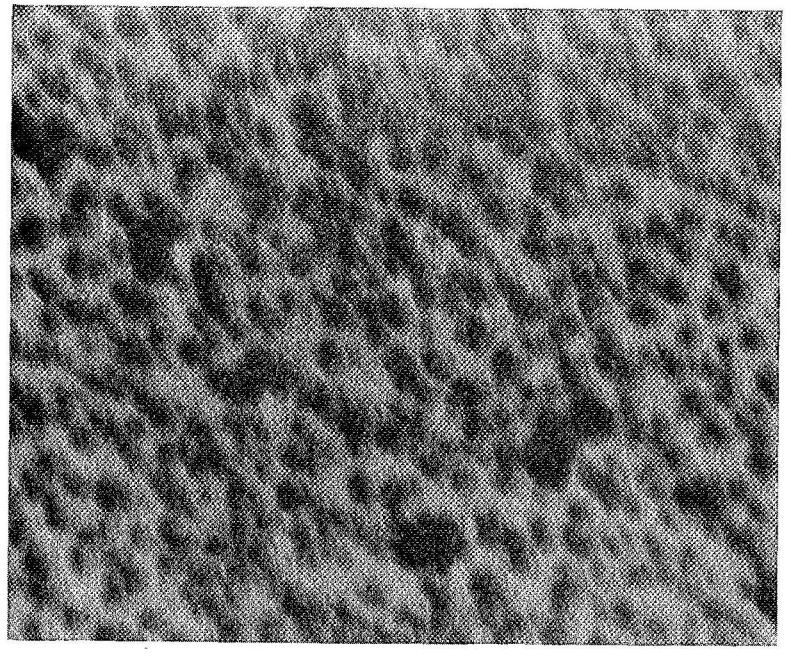

Fig. 3. Surface replica of lithium doped (10^{17} atoms/cm^3) silicon solar cell X35,000

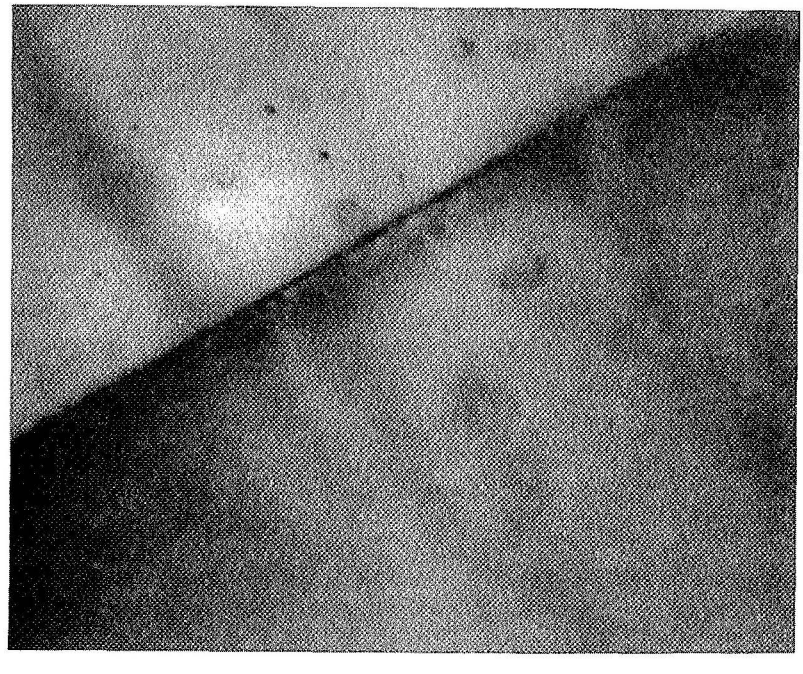

Fig. 4. Thin film transmission photograph of undoped silicon solar cell X25,000

very flat defect free region with very little structural detail, with the exception of a grain boundary which runs diagonally across the photograph. In the transmission photograph from the doped material, Figure 5, however, numerous small structural defects can be observed throughout the field, which are indicative of the presence of precipitate particles.

Further evidence for the presence of precipitate particles in the doped material is provided by careful examination of the electron diffraction patterns from the doped and undoped thin film samples. Figure 6 shows the diffraction pattern obtained from the undoped sample. The only diffraction spots which can be observed are those which one would expect from the diamond cubic lattice of silicon. An interpretive schematic drawing of the above diffraction pattern with each spot indexed is shown in Figure 7 (a). In Figure 8, however, which shows the diffraction pattern obtained from the doped sample, a number of additional, but weaker spots can be seen. An interpretive drawing of this diffraction pattern is shown in Figure 7 (b). In this particular pattern the additional diffraction spots can only be indexed satisfactorily as belonging to the bcc crystal structure. Assuming the lattice parameter of silicon it is possible to calculate the lattice parameter of the bcc structure by comparing the radius ratios of the selected area diffraction spots. From such a calculation, the lattice parameter of the bcc crystal structure was found to be 3.45 Å which agrees very well with that for lithium. From this evidence it appears that the precipitate particles observed in the doped silicon cells are probably due to excess lithium. From Figure 7 (b) it can be seen that the $2\bar{2}0$ planes of the precipitate are almost parallel (within 5°) to the 220 planes of the silicon matrix.

The effective macroscopic cross section for the electron diffraction was approximately 5 microns squared. From a diffraction pattern such as this, it is impossible to estimate the specific number of microcrystallites of the precipitated phase which are giving rise to the additional diffraction spots. Therefore, it is not possible to measure the density of the precipitates from selected area diffraction.

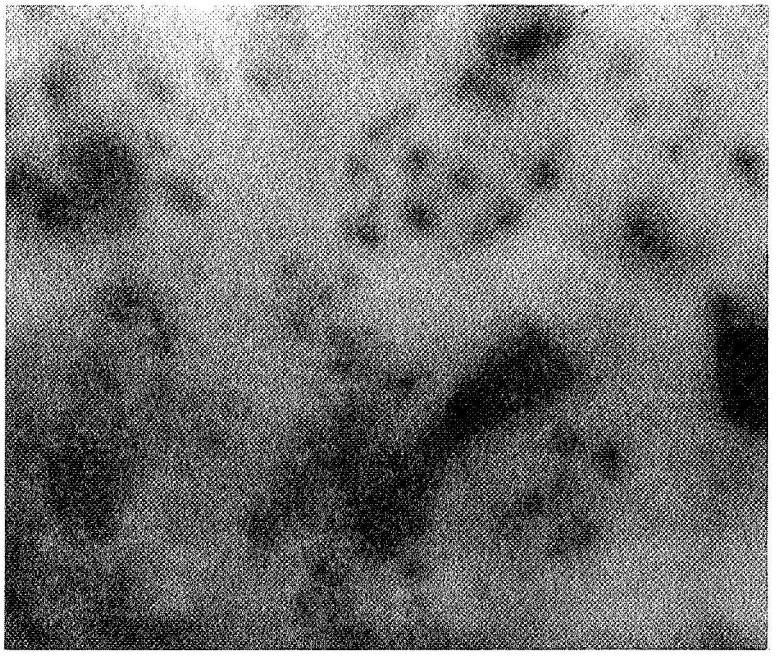

Fig. 5. Thin film transmission photograph of lithium doped (10^{17} atoms/cm^3) silicon solar cell X25,000

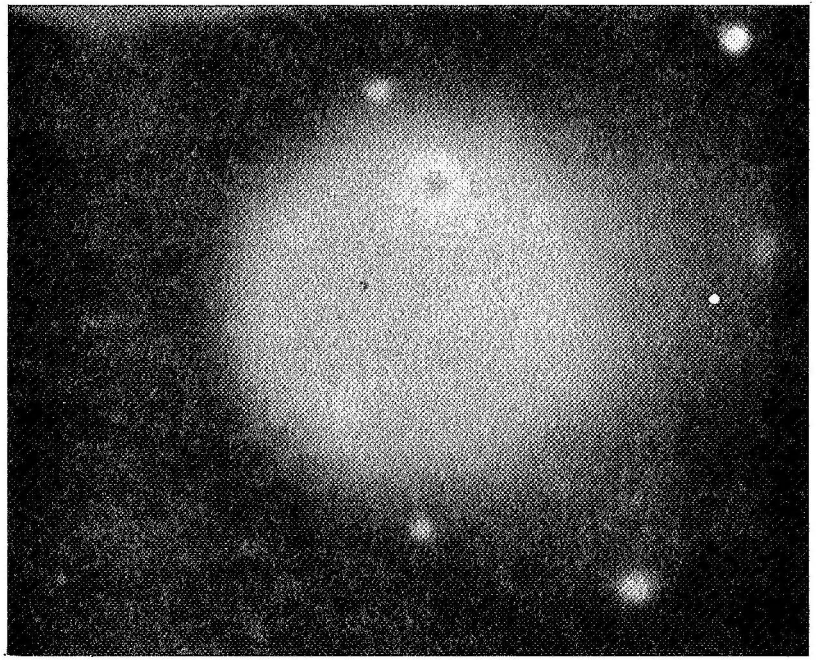

Fig. 6. Electron diffraction pattern from thin film of undoped silicon solar cell.

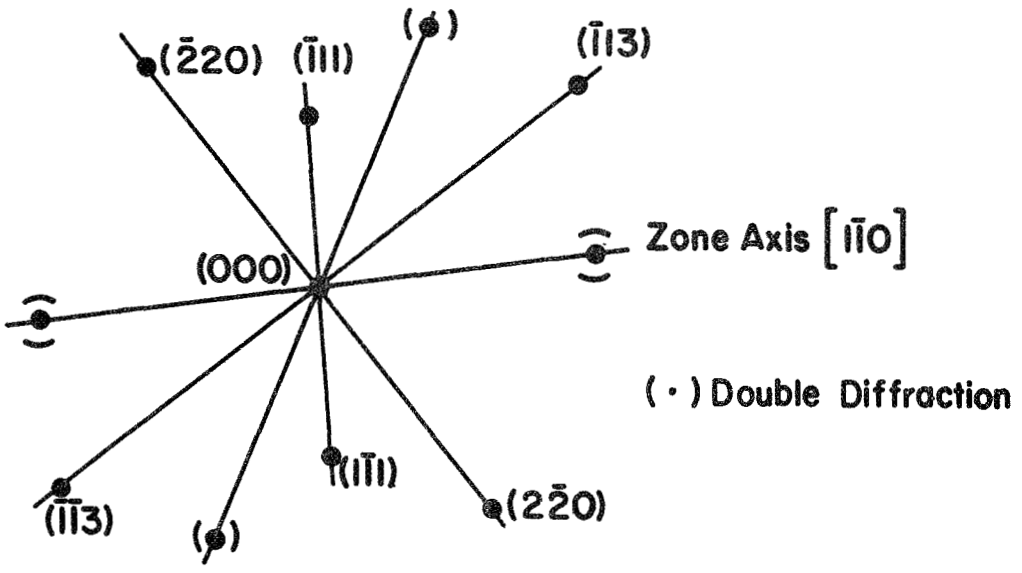

Fig. 7 (a). Interpretation of the diffraction pattern shown in Figure 6.

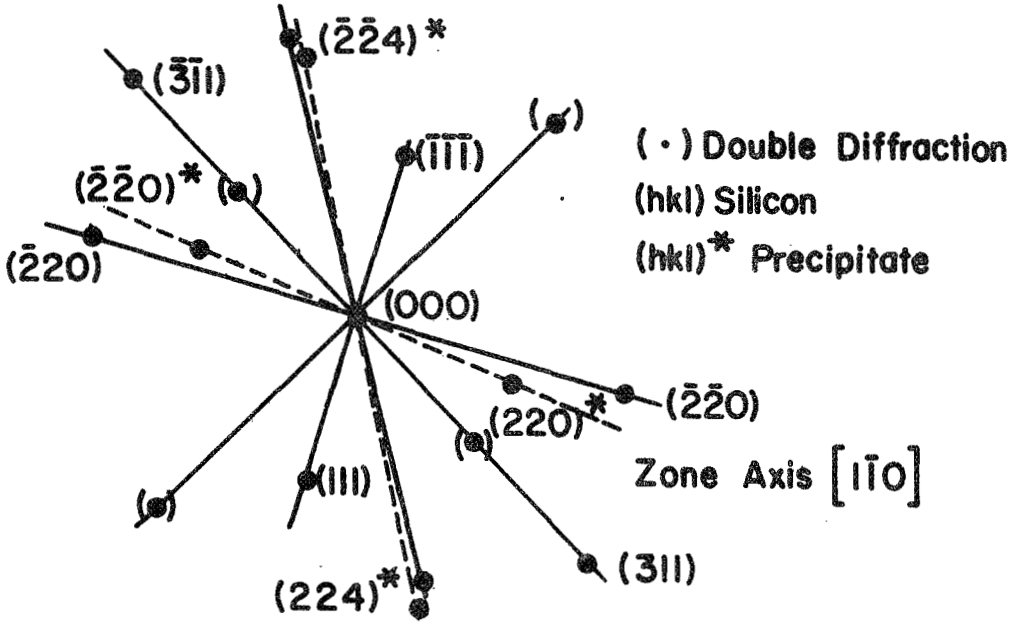

Fig. 7 (b). Interpretation of the diffraction pattern shown in Figure 8.

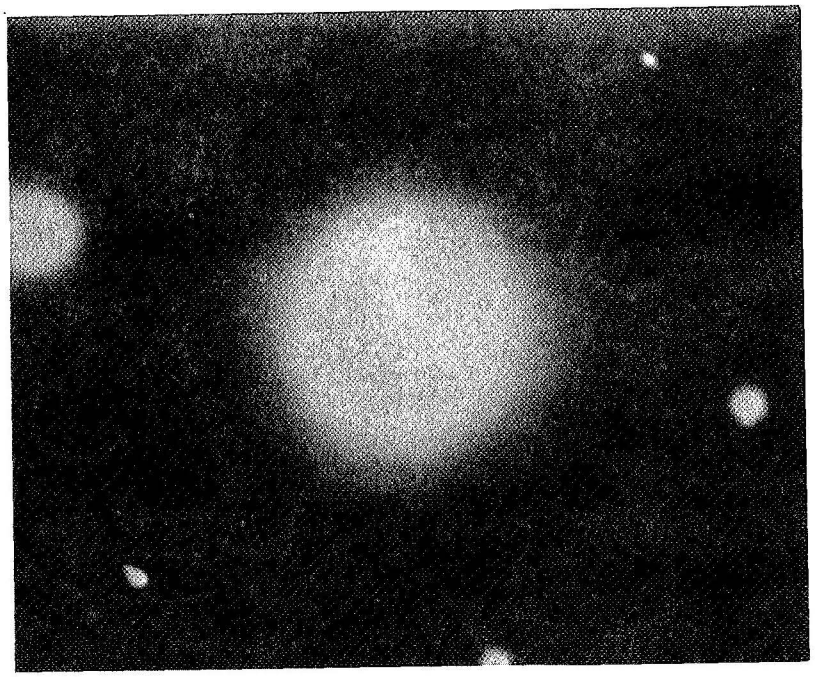

Fig. 8.. Electron diffraction pattern from thin film of lithium doped (10^{17} atoms/cm^3) silicon solar cell.

Conclusions

1. Techniques have been established to etch and observe undoped and lithium doped silicon solar cells by surface replication and by thin film transmission electron microscopy.
2. From preliminary surface and thin film observations it appears that a second phase precipitate exists in the doped cells which has a bcc crystal structure and has a lattice parameter close to that of lithium. Therefore, as lithium is the only bcc material present in any large amounts, it seems reasonable to conclude that in fact the precipitates are formed from excess lithium. (The above observations are in agreement with the results of Berger, Horiye, Naber, and Passenheim [19]. Recently they have carried out a neutron activation analysis of lithium doped cells in which resistivity measurements had indicated a lithium concentration of 10^{17} atom/cm^3, and in fact, they found that activation analysis indicated a concentration up to eight times greater than this. They suggested the possibility that some lithium may be present as precipitates).

Plans for the Next Reporting Period

During the next reporting period we plan to:

1. Irradiate undoped and doped lithium solar cells.
2. Study defects produced by neutron irradiation using surface replication and thin film transmission electron microscopy.
3. Anneal the irradiation damage.

New Technology

No new technology is currently being developed or employed in this program.

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