Effect of electron irradiation on dark and photoconductivity of amorphous hydrogenated silicon

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The dark conductivity of amorphous hydrogenated silicon is found to increase immediately after electron irradiation. The conductivity decreases as a function of time and settles at a value lower than the original one after room-temperature annealing for 12 h. The photoconductivity is also found to be lower. Annealing at 200 °C is found to restore the dark and photoconductivity to their original magnitude. The results are discussed in terms of dangling bonds and vacancy-impurity complexes created by irradiation.

I. INTRODUCTION

There has been a great deal of interest in the study of amorphous hydrogenated silicon (*a*-Si:H) prepared by the glow-discharge decomposition of silane as a potential solar cell material. Earlier experiments[1,2] on vacuum deposited amorphous silicon films showed that the electrical conductivity of these materials is rather insensitive to electron irradiation. This is due to the presence of a large number of gap states in these films[3] and it has been shown[4,5] that in glow-discharge films which have very few states in the gap, electron irradiation causes defects which increase the spin density and quench the band-edge photoluminiscence. We have carried out experiments to study the effects of electron irradiation on the dark dc conductivity and photoconductivity of *a*-Si:H films. The results are reported in this paper.

II. EXPERIMENTAL DETAILS

The samples were made by dc discharge of 10 mol% SiH_4–90 mol% H_2 mixture at a pressure of 0.5 torr and substrate temperature of 300 °C. The details of sample preparation and characterization are discussed elsewhere.[6,7] Substrates used are Corning 7059 glasses with predeposited NiCr contacts spaced 1 mm apart and typical film thickness is between 6000 Å and 1 μm. Electron irradiation was performed using Tata Institute of Fundamental Research (TIFR)-pulsed linear accelerator. The electron beam of energy 3.5 MeV was pulsed at 20 cps, the width of each pulse being 2 μs. Electrons of energy 3.5 MeV have a projected range[8] in silicon of several millimeters and defects are therefore distributed uniformly throughout the sample. The energy used is also well above the threshold energy for electron damage which is about 100 keV for crystalline silicon and about 1 keV for *a*-Si:H.[9] Irradiation was carried out for 30 min and this corresponds to an electron dose of 2×10^{15} cm^{-2} on the sample as measured by a current integrator. The sample holder was evacuated to 10^{-2} torr using a sorption pump and the samples were annealed at 200 °C for 2 h before any irradiation was done. All measurements were carried out *in situ*. The photoconductivity was measured with a sodium lamp or with a defocused He-Ne laser beam. Results obtained were similar for the two types of sources. The power incident on the sample was measured with a thermopile detector. For measurements of dependence of photoconductivity on intensity, the incident power was varied by using suitable neutral density filters.

III. RESULTS

Figure 1 shows the dependence of the dark conductivity of a sample as a function of time immedi-

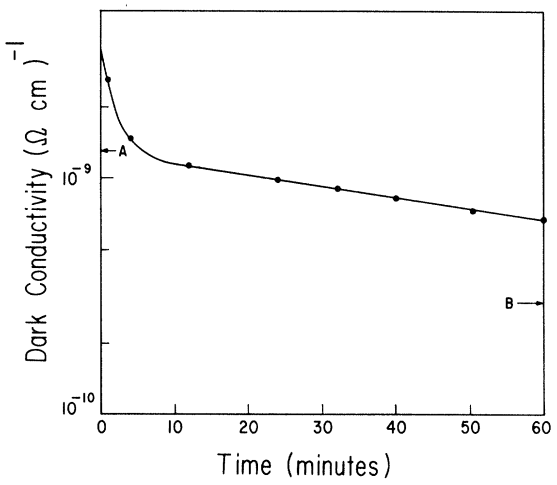

FIG. 1. Time dependence of dark conductivity measured *in situ* immediately after irradiation. *A* and *B* refer, respectively, to the values before irradiation and after irradiation and subsequent annealing at room temperature for 12 h.

ately after irradiation. We see that at time $t=2$ minutes after irradiation, the conductivity is larger than the initial value and slowly settles at a value below that of the original conductivity.

Figure 2 shows the intensity dependence of the photoconductivity before irradiation and after storing the sample in vacuum at room temperature for 12 h. On the intensity scale, $I=1$ corresponds to an intensity of 50 μW/cm^2 incident on the sample from a sodium lamp. In order to calculate the photoconductivity, we have not corrected for reflection or absorption losses. We see that the photoconductivity varies as $\sigma_{ph}=AI^{\nu}$ where $\nu\sim 0.8$ both before and after irradiation. The magnitude of the photoconductivity at $I=1$ has decreased by about a factor of 16 after irradiation. Annealing at 200 °C for about 6 h in vacuum restores both the dark and photoconductivity to their initial values.

Although most of the samples investigated show the trend of an increase in dark conductivity immediately after irradiation and a decrease in both dark and photoconductivity subsequent to irradiation and room-temperature annealing, the exact magnitude of the change differs from sample to sample. In Table I we present results for several samples which show a scatter in the values of dark and photoconductivity typically observed in undoped films. In general, we find that immediately after irradiation the dark conductivity is higher and it settles down at a value lower than the initial conductivity after about 12 h. In the case of sample 1, the annealing time at room temperature required for the dark conductivity to go below the initial value is slightly higher. Moreover in this sample the initial change in dark conductivity as a result of irradiation is also much larger. We also note that although for most of the samples the value of ν is about the same both before and after irradiation. Sample 3 shows an increase in ν after irradiation.

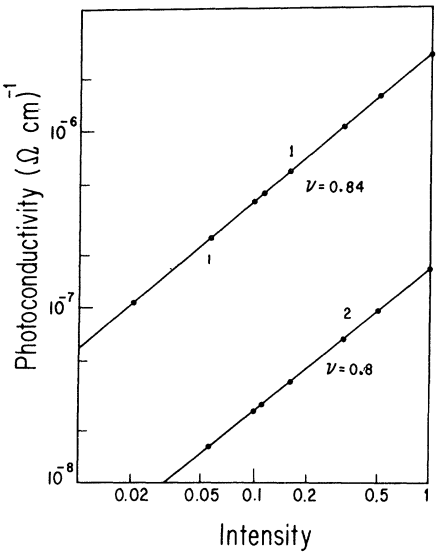

FIG. 2. Dependence of photoconductivity on intensity (1) before irradiation (2) after irradiation and subsequent annealing at room temperature for 12 h.

In order to establish that the changes in dark conductivity are not caused by charged centers in the substrate created by irradiation, we have studied the effect of electron irradiation on a Pd-Schottky diode prepared on *a*-Si:H. The series resistance of the diode was found to increase by a factor of 2 after irradiation and subsequent storing at room temperature for 12 h. This is in agreement with the results obtained in the planar structure indicating that the observed changes in conductivity reflect bulk changes.

TABLE I. Results for various samples. σ_{di} = initial dark conductivity; σ_{phi} = initial photoconductivity; $\Delta\epsilon$ = activation energy; σ_{df1} = dark conductivity 2 min after irradiation; σ_{df2} = dark conductivity 12 h after irradiation; σ_{ph2} = photoconductivity 12 h after irradiation; and ν_i, ν_{f2} = initial and final value of exponent ν. Intensity on the sample for Na lamp is 50 μW/cm^2 and for laser is 160 μW/cm^2.

Sample	1	2	3	4	5
$\sigma_{di}(\Omega^{-1}\text{cm}^{-1})$	6.7×10^{-9}	1.3×10^{-9}	1.2×10^{-8}	1.5×10^{-7}	3.5×10^{-9}
$\sigma_{phi}(\Omega^{-1}\text{cm}^{-1})$	1.8×10^{-5}	2.8×10^{-6}	5.10^{-6}	1.3×10^{-5}	1.10^{-5}
$\Delta\epsilon$(eV)	...	0.6	0.6	0.56	...
σ_{di}/σ_{df1}	3.5×10^{-2}	0.5	1.2	1.05	0.23
σ_{di}/σ_{df2}	1	4	2.7	1.5	1.7
$\sigma_{phi}/\sigma_{phf2}$	10	16	8.5	8.5	4
ν_i	0.75	0.84	0.64	0.6	0.3
ν_{f2}	0.72	0.8	0.79	0.6	0.8
Light used	Laser	Na lamp	Na lamp	Na lamp	Na lamp

IV. DISCUSSIONS

High-energy bombardment by electrons creates damage by direct displacement of atoms from their defined lattice sites. Since the projected range of the 3.5-MeV electrons is much larger than the thickness of the samples, a uniform distribution of point defects is expected to be created[4] by electron irradiation. When a silicon atom is removed from the lattice site, four dangling bonds are created and in crystalline silicon,[10] they rearrange at room temperature to form divacancies giving rise to well-defined states in the gap. In addition, it has been seen in crystalline silicon that the irradiation-produced defects can form complexes with the various impurities present in the material giving rise to a host of other levels[11] within the gap. The problem of impurity is especially acute in amorphous hydrogenated silicon[12] which contains hydrogen (5 to 30 at.%), oxygen (0.1 to 0.5 at.%) and also traces of nitrogen and carbon. The presence of large concentration of hydrogen implies that we must consider collisions with both silicon and hydrogen. A missing hydrogen results in a single dangling bond with no reconstruction and this may have its bonding and antibonding states within the gap.[13] If hydrogen is present in the form of dihydrides, removal of two hydrogen atoms may lead to reconstruction[14] and could give rise to additional levels. With such a complexity in the distribution of the states in the gap produced by electron irradiation, it is not possible to explain the experimental results quantitatively and we shall make only some general observations. Creation of a large number of states near the Fermi level will cause an increase in hopping conduction and this may account for the initial rise in conductivity after irradiation. Alternatively, there may be an increase in conductivity if the Fermi level shifts slightly closer to the conduction-band edge. Since the position of the Fermi level in this material is essentially determined by the overlap of the donor-acceptor states,[15] creation of new states can easily shift the Fermi level downward or upward in the gap. The states that give rise to the enhanced conductivity anneal out at room temperature. We suspect that these are due to oxygen-related defects since sample 1 which showed a large increase in conductivity also had a larger oxygen content ($\sim 1\%$) as estimated from IR absorption measurements. Further experiments on samples with varying amount of oxygen will be necessary to establish the role of oxygen-related defects unambiguously.

There is another set of defects which are stable at room temperature and can be annealed out only at 200 °C. These defects push the Fermi level slightly downward resulting in a decrease of conductivity. The photoconductivity is also lowered. Since the photoconductivity is found to vary with intensity as $\sigma_{ph} \propto I^{\nu}$ with ν close to 0.8, one can use the model developed by Rose[16] to explain the data. In this model, the material is supposed to have both trapping and recombination centers with essentially the states lying between the dark Fermi level E_F and the quasi-Fermi level E_{Fn} acting as the recombination centers. The exponent ν reflects the energy distribution of these centers. We note that ν does not change very much on irradiation whereas the magnitude of photoconductivity has reduced. If the capture cross sections of the new defect centers caused by irradiation are the same as those for the recombination centers originally present in the material, this implies that the irradiation-induced defects give rise to new states distributed between E_F and E_{Fn}. Since the activation energy is 0.6 eV we conclude that the new states are distributed slightly above this energy. It is interesting to note that the 0.9-eV luminiscence in irradiated *a*-Si:H has been attributed[17] to a defect level about 0.5 eV from the conduction-band edge. It is believed that a dangling bond as described earlier is responsible for this defect.

A reduction in dark and photoconductivity has also been observed in *a*-Si:H after prolonged exposure to light.[18,19] The origin of this effect is still not clearly understood. Staebler and Wronski[19] show that bulk changes take place as a result of light exposure and recent ESR measurements by Dersch *et al.*[20] indicate that the light-induced defect centers are single dangling bonds. In that case, the electron-induced and the light-induced defects are similar. One also notes that photoluminiscence measurements[21,22] also suggest similarity in defects induced by strong light exposure and electron irradiation since both give rise to centers responsible for luminiscence in the energy range 0.8 to 0.9 eV. There must also be defect centers which are not common for the two cases since unlike electron irradiation, light exposure has been found to cause a vary large decrease in dark conductivity. It is interesting to note that results in our laboratory[6] and at Dundee[23] show that the change in dark conductivity induced by light exposure is quite small. If the photoinduced defects are created by the breaking of weak Si—Si bonds, one wonders if the above results imply that the bonds are stronger in these materials in which case they may be more stable to electron irradiation also, especially at lower energies. On the other hand it is also possible that impurities present in these materials favor formation of vacancy-impurity complexes with energy levels located such that there is no appreciable effect on dark conductivity. The observed scatter in the data shown in Table I is then somewhat analogous to the large variation in light-induced effects observed in different laboratories (or often in different films prepared in the same laboratory). We have shown elsewhere[24] how traces of phosphorus can change the nature of the defects produced by electron irradiation.

In conclusion, we have studied the effect of elec-

tron irradiation on the dark and photoconductivity of amorphous hydrogenated silicon. We find two sets of defects with different annealing behavior. The first set increases the dark conductivity and anneals out at room temperature. The second set of defects causes a decrease of dark and photoconductivity and can be annealed out only after heating at 200 °C. The results are discussed in terms of dangling bonds and impurity-vacancy complexes created by irradiation.

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