ELECTRON-BEAM INDUCED CENTERS IN HYDROGENATED AMORPHOUS SILICON
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Abstract.—Photoluminescence was used to compare the effects of low-energy electron bombardment and laser irradiation in a-Si:H. The main effects are similar: 1) decrease of the main luminescence peak at 1.2 eV, 2) enhancement of luminescence at 0.8 eV, and 3) complete recovery of the original properties after annealing at 200°C. The decrease at 1.2 eV however, is much more pronounced with electron than with photon irradiation.

I. Introduction.—Electrical and optical bulk properties of hydrogenated amorphous silicon (a-Si:H) are affected by photon- (1,2,3), as well as by electron- and ion-irradiation (4). With regard to electron-induced property changes, so far only 1 MeV electron irradiation has been studied (4). We have reported recently (5) that undoped a-Si:H can be damaged by electrons at much lower energies than crystalline silicon, with a damage threshold energy below 1 keV. The penetration depth of electrons with a few keV is of the order of 100 nm (6), and it is thus comparable to the penetration of photons in the visible range. With about equal penetration of photon- and electron-irradiation, a close comparison of their effects can be made; based on photoluminescence and annealing measurements, we will provide evidence that the nature of defects generated by either photons or electrons is very similar.

II. Experiments.—The samples were undoped a-Si:H deposited on stainless steel or crystalline silicon by glow discharge decomposition of silane. The hydrogen concentration determined by secondary-ion mass-spectroscopy (7) was 5 to 7 x 10²¹ cm⁻³. The electron irradiation was performed at room temperature in a scanning Auger microprobe system, using electron energies between 1 and 5 keV, and an electron dose of typically 1 x 10¹⁸ electrons/cm². The photon-irradiation occurred at room temperature or elevated temperatures (up to 100°C) using an argon laser (488 nm) at a dose of about 3 x 10²¹ photons/cm². Both types of irradiation were applied to similar samples, or even side-by-side to the same sample. Damage profiling, by using a combination of scanning Auger microprobing and Ar⁺-sputtering (5), clearly shows that in both cases the irradiation has affected the bulk of the sample, rather than just the surface. The depth of damage as a function of the electron energy is shown in Fig. 1; the electron penetration agrees well with that obtained from range-energy relations (6). The photon penetration was determined by damage profiling to be

Fig. 1. Maximum depth of damage as a function of the electron irradiation energy for four different undoped a-Si:H samples. The dashed curve indicates an average.

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Fig. 2. Photoluminescence intensities at 1.2 eV (upper two curves) and 0.8 eV (lower two curves) across a photon- and electron-irradiated samples. Solid lines: after irradiation; dashed lines: after partial anneal.

200 nm; this value closely corresponds to the inverse absorption constant of a-Si:H at 488 nm (8).

The photoluminescence (PL) was measured at 77 K, with the exciting beam at a sufficiently low dose to avoid irradiation damage during the measurement. The sample could be translated in the focal plane of the spectrometer to scan the luminescence intensity and compare the irradiated and non-irradiated regions on the same sample. Figure 2 shows traces through electron- and laser-irradiated regions, at the luminescence peak at 1.2 eV, and at 0.8 eV, following irradiation and a partial anneal (see below). Figure 3 shows the spectral dependence of the PL before and after electron-irradiation. The main peak at 1.2 eV always drops in intensity after irradiation, typically by 15% after photon-irradiation, and by about 90% after electron-irradiation. At about 0.8 eV, the changes in PL are similar for both photon- and electron-irradiation. While after photon exposure one always finds an increase at 0.8 eV, electron exposure may result in either an increase (as shown in Fig. 3) or a decrease of the PL intensity. As shown in Fig. 2 and further discussed below, the 0.8 eV emission can be turned into an enhancement by a slight anneal.

At room temperature, some annealing of the irradiation-induced defects occurs over a period of several months. Isochronal annealing (5 min periods) of a sample that contained both photon- and electron-damage resulted in a gradual disappearance of the irradiation-induced effects. Thus, Fig. 4 shows that the original intensities at 1.2 and 0.8 eV are recovered at about the same annealing temperature of 230°C. In the case of electron-irradiation, we observe a transition of the 0.8 eV intensity from a decrease to an increase before the final recovery. A similar increase of PL at about this energy has also been observed after low-temperature anneals at about 100°C on samples irradiated with 1 MeV electrons (4).

Secondary-ion mass-spectroscopy shows that the irradiation-induced changes are not related to a loss of hydrogen, and this is further evidenced by the full recovery of the original PL intensity after annealing.
III. Discussion.— Our experiments cannot give direct information on the atomic structure of the defects introduced by either photons or electrons. However, the following conclusions with regard to their properties can be reached.

For photon-induced defects we must postulate that they are caused by electronic excitations, since no direct momentum transfer can occur. For electron irradiation, energy and momentum can give rise to direct atomic displacements. But the low-damage-threshold energy found for a-Si:H (5) would account at most for the atomic displacement of hydrogen. Experiments with a-Si:D, however, have led to the same low-damage-threshold energy (9). Therefore, in the case of electron-irradiation, we can rule out direct atomic displacements of hydrogen. Instead, electronic excitations may lead to changes in certain bonding configurations.

Our tentative model for the mechanism of defect formation is that irradiation breaks the weaker bonds between Si atoms. Those are the bonds between atoms that are farther apart than in a crystal, or bonds the steric conformation of which is not optimally tetrahedral. Such bonds are already prestressed and require less energy for dissociation.

For electron-induced defects, the depth of damage after a given electron energy and dose increases with the hydrogen content of the sample (9). Hydrogen thus plays a role in the nature of the damage. But we cannot distinguish, whether Si-H bonds are directly involved, or whether Si-Si bonds close to Si-H bonds are broken more easily, as has been suggested (3,10). Note that since the Si-H bond is stronger than the Si-Si bond (11), it is less likely that irradiation would ionize the Si-H. This explains the stability of the H concentration, as evidenced by the secondary-ion mass-spectroscopy results and by the complete recovery of PL upon annealing.

In an amorphous material, there is a large range of binding energies. Blue light provides at most 2.5 eV to the dissociation process. The low-energy electron irradiation, on the other hand, provides multiple, and possibly more energetic excitations. Therefore, provided the cross-sections for electron- and photon-produced defects are not vastly different, comparable damage can be generated at a much smaller electron than photon dose. The larger drop in PL at 1.2 eV after electron irradiation, compared to photon irradiation, may be due to more energetic excitations that result in a broader range of bond breaking. From the PL results we conclude that at least two different defect centers are involved: 1) non-radiative center, causing a reduction of the main peak at 1.2 eV, and 2) deep gap-states,
opening new radiative recombination paths at energies around 0.8 eV, and thus accounting for the observed increases in PL.

It is believed that the non-radiative centers are related to the Staebler-Wronski effect (2) which greatly lowers the room temperature dark conductivity after exposure to light. Presumably, the carrier lifetime is greatly reduced by the newly formed recombination centers. Such recombination centers would be expected to adversely affect the performance of solar cells.

As to the nature of the 0.8 eV luminescent center, its identification will require further study. Its energy suggests a mid-gap state ($E \approx 1.6$ eV). Deep centers, by virtue of their strong localization, can be efficient radiators. It appears that these centers responsible for the PL increase at 0.8 eV are the result of a temperature-assisted rearrangement of irradiation-affected bonds that occurs either during the irradiation, or thereafter. Thus the enhancement of the 0.8 eV PL is observed always after photon-irradiation and sometimes after electron-irradiation. However, when the emission at 0.8 eV is decreased after electron-irradiation, a slight anneal transforms the decrease into an increase (see Fig. 4 and (4)).

IV. Conclusion.— Both electron- and photon-irradiation produce two types of centers: non-radiative centers that are dominant, and radiative centers that emit at about 0.8 eV. The behavior of these centers is as follows: 1) The spectral dependence of the PL is affected similarly by electron- and photon-irradiation, namely, a decrease of PL intensity at the emission peak and an increase of the PL intensity around 0.8 eV. 2) The temperature history leading to the PL intensity increase at 0.8 eV is similar, namely, a moderate heating (to ~100°C) during irradiation (1), or later during annealing; enhances the increase. 3) Full recovery of the PL intensity is obtained at the same annealing temperature after both electron- and photon-irradiation.

V. References.—