Light Induced Creation and Annealing of Metastable Defects in Hydrogenated Amorphous Silicon

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Received September 9, 1993

We report on the decrease of tlie defect density induced by continuous illumination after fast clefect creation by pulsed light. The kinetics of creation and recovery of metastable defects are discussed, as well as the implications for present models treating metastable defects in hydrogenated amorphous silicon.

I. Introduction

Hydrogenated amorphous silicon (a-Si:H) is a. technologically important material[1]. Tlie special attribute of a-Si:H which makes it useful is the ability to deposit the material unexpensively over large areas, while retaining good semiconducting properties (low density of the intrinsic Si dangling bond defects). On the other hand, its potential applications have been severely limited by the existence of structural metastabilities wliicli occur when a-Si:H is electronically excited for extended periods of time. The most notorious example is the creation of metastable defects states in undoped a-Si:H by prolonged illumination, tlie so called *Staebler-Wronski effect*[2]. Light-induced reversible structural changes in amorphous silicon are a fundamental problem which is poorly understood on a microscopic level[3]. One of the most controversial points is the observation of an apparent saturation in the density of light-induced defects[4-6] which has important implications for the origin of the metastability. Saturation can either be viewed as evidence for a finite number of sites which can be converted into defects (e.g. impurities[7]), or as an equilibrium between defect creation and annealing[5,6]. Various rnodels have been proposed for the kinetics of defect. creation and annealing[3]. Despite of the inclusion of a light-induced recovery of defects in some theories[7], only recently light-induced recovery of defects has been observed[8]. This article descrihes in detail experimental results concerning the Itinetics of defect creation and annealing induced by illumination.

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II. Experimental

Tlie samples used in this study were deposited by glow discharge of silane under standard conditions for device quality material. The change in the density of metastable defects was monitored by measuring the photo-conductivity and the electron-spin-resonance (ESR) of the silicon dangling bond.

For tlie photo-conductivity measurements, 0.7 μm thick samples were used. Two types of illumination were employed: continuous illumination with a tungsten halogen lamp ("cw"), and light pulses with a xenon flash lamp ("A") with a. pulse width of = 2 fs and a. pulse repetition rate of 300 Hz, leading to an average illumination intensity of 100 mW cm^{-2} . The time-clependence of the plioto-conductivity was monitored with homogeneously absorbed light ("cw" light + RG630 filter), with an illumination intensity of 3 mW cm^{-2} . The sample temperature variations were kept below 2 °C during the measurements. Temperature calibration was performed using a 0.5 μm thick a-Si:H film grown over a low heat-capacity Ni resistor thermometer. The defect density (N) was calculated from the

photo-conductivity (σ_{ph}), as $\sigma_{ph} = C/N$. The validity of this relation, and tlie constant C (10^{10} cm^2 Ω^{-1}) had been previcusly found for "fl" soaked samples[9]. This relation ho.ds for defect densities higher than $5x10^{16}$ cm^{-3}.

For the ESR measurements, 1.6 μm thick samples were used. Metastable defects were created by a Cu-vapor-laser at 511 nm using liglit pulses with a.duration of = 20 ns and a pulse repetition rate of 7kHz, yielding an averiage illumination intensity of 500 mW cm^{-2}. The light-a.nealing was done by an Ar+ -ion laser at 514.5 nm, with an intensity of 60 mW cm^{-2}. For this experiment tlie sample temperature was kept below 20° C. The reversibility of all light-induced defects was verified by annealing at 180° C for 4h.

III. Results and discussion

Data foi the light-induced annealing of defects are shown iii Fig. 1. After illuminating tlie sample with "fl" ligl^{g}it foi 12000 s, the photo-conductivity dropped from $9.5x10^{-7}$ to $5.5x10^{-7}$ (R cm)$^{-1}$. By changing the illumination from pulsed light to "cw" light (50 mW cm^{-2}), the photo-conductivity increased again to $8.5x10^{-7}$ (Ω cm)$^{-1}$ (i.e. approximately a.50 % cliange), after 150000 s (triangle). Thermal effects are ruled out since, for the same temperature a. negligible change in the photo-conductivity is observed when tlie sample is left in the dark (crosses). For comparison, tlie light-induced degradation of tlie photo-conductivity using tlie same light intensity is also plotted (circles). Both curves approach a steady state photo-conductivity of approximately $1.1x10^{-6}$ (R cm)$^{-1}$.

In order to clearly observe tlie phenomenon of light-induced annealing, great care lias to be taken to minimize thermal annealing effects. Results on thermal annealing of clefect obtained from photo-conductivity measurements are shown in Fig. 2. The creation of defects by "fl" and "cw" illumination are represented by the filled dots. The results indicate that thermal annealing is negligible when the sample is kept at 20°C or below but starts to be significant at temperatures of 30°C and higher. To avoid the intermixing of light-induced and thermal annealing, all light-induced annealing experiments were performed at 20°C or below.

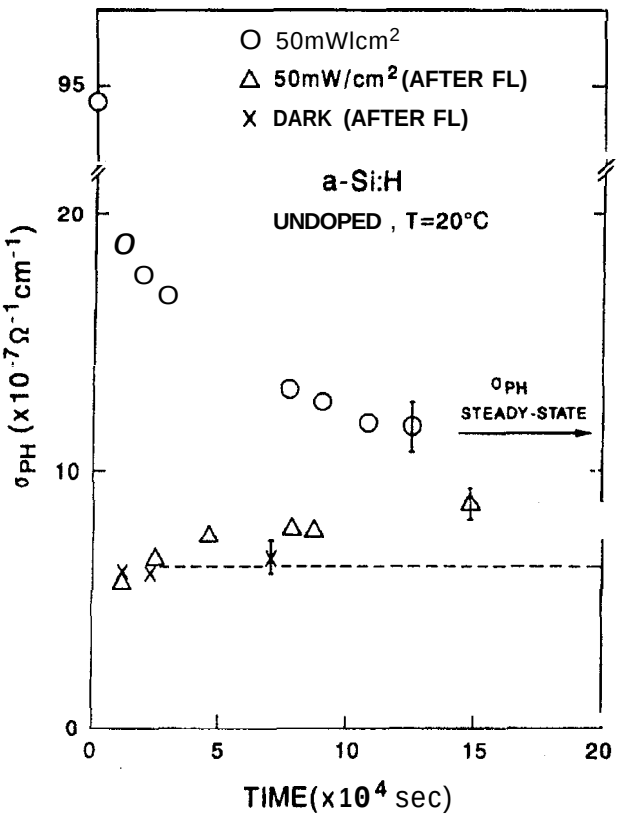

Figure 1: Photo-conductivity clianges due to the light-induced creation and annealing of defects: (circles) light-induced creation with "cw" illumination; (triangles) light-induced annealing with "cw" illumination after fast creation of defects by "fl" illumination. A negligible thermal annealing is observed at 20°C (crosses). Tlie arrow on the right edge represents tlie calculated steady-state value for tlie photo-conductivity using the solution of Eq. 1.

Two initial defect densities were used for the light annealing experiments: $1.6x10^{17}$ and $3.1x10^{17}$ cm^{-3}. In Fig. 3, the depenclence of light-induced annealing on initial defect densities and on illumination intensities are presented. Tlie lines are theoretical fits to the data points discussed in the following. For low initial defect density, we notice that as the illumination intensity increases, the light-induced annealing effect seems to be smaller. In fact, the largest decrease in the defect density is observed for illumination intensities of 50 mW cm^{-2}, while practically no change is observed for 200 mW cm^{-2}. For the experiments with a higher ini-

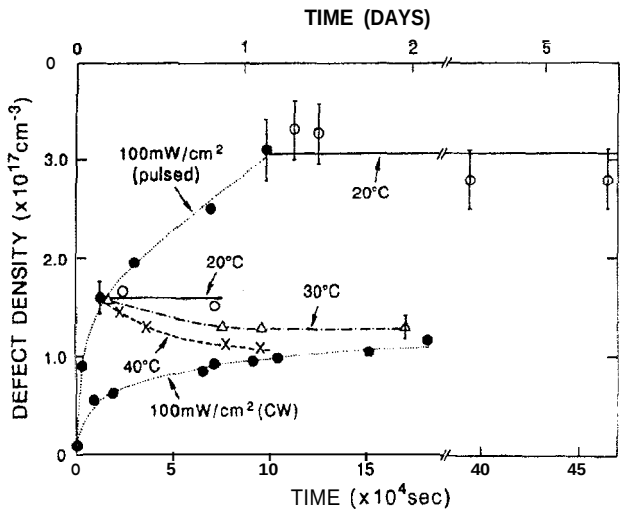

Figure 2: Defect density changes as obtained from photoconductivity measurements for: (filled circles) light-induced creation using "fl" and "cw" illumination; thermal annealing of defects after "fl" illumination at 20°C (open circles), 30°C (triangles) and 40°C (crosses). The plotted lines are guides to tlie eye.

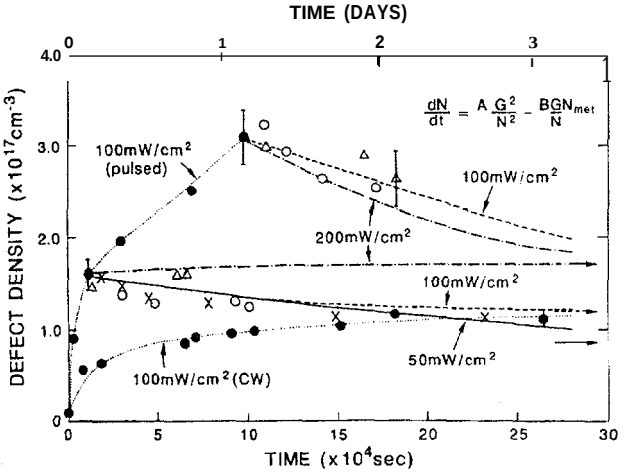

Figure 3: Defect density changes as obtained from photoconductivity measurements for: (filled circles) light-induced creation of defects using "fl" and "cw" illumination: light-induced annealing of defects using "cw" illumination with different intensities, 50 mW cm^{-2} (crosses), 100 mW cm^{-2} (open circles) and 200 mW cm^{-2} (triangles). Also plotted as lines, are tlic theoretical fits to tlie data points for tlie solutions of Eq. 1, as a function of illumination intensity. Tlie calculated steady state defect density as a function of illumination intensity are indicated by arrows at tlie right edge of the figure.

tial defect density, no clear dependence on illumination intensity is observed within experimental accuracy. We would like to point out here that the large error bars are mainly due to the long illumination and annealing periods over several days anil the small relative changes of tlie coplanar conductivity.

As discussed elsewhere[10], thc kinetics of light-induced degradation using pulsed light cannot be explained with models involving linear or sub linear carrier-density dependence of the defect creation rate[7,11]. Based on this experimental fact, a reasonable extensions to the model of Stutzmann, Jackson and Tsai[12] is presented.

In tliese extension the light-induced annealing term is -BGN$_{met}$/N, where N$_{met}$ is the density of metastable defects, and G the generation rate of free carriers. The underlying idea is thnt tlie capture of excess electrons (or holes) with density $n(\overline{p}) \propto G/N$ into metastable dangling bonds triggers the light-induced annealing of the latter. In our case, since to a good approximation $N_{met} \approx N$, this term is siinply -BG. In this case:

$$\frac{dN}{dt} = A\frac{G}{N} - BG \qquad (1)$$

where t is the time. From the steady-state condition dN/dt=0, one find $N_{ss} = (AG/B)^{1/2}$.

The constants A and B are fitting parameters. From the experimental results in Fig. 3, N_{ss} for 100mW cm^{-2} "cw" illumination is estimated to be 1.2x10^{17} cm^{-3}, so that in reality, only one parameter in Eq. 1 is free to adjust. The least square fit of the experimental data. to Eq. 1 is plotted in Fig. 3 (A = 11500 cm^{-3} s). A good agreement is found witli the experimental data.

Finally, one could imaging that the same two-carrier process causing defect creation also could give rise to tlefect annealing. In this case however it is easy to see that the steady-state defect density would be independent of light intensity, contrary to the experimental results. Therefore this possibility can be ruled out.

The light-induced annealing of metastable defect was also observed in tlie ESR. signal iiitensity of the

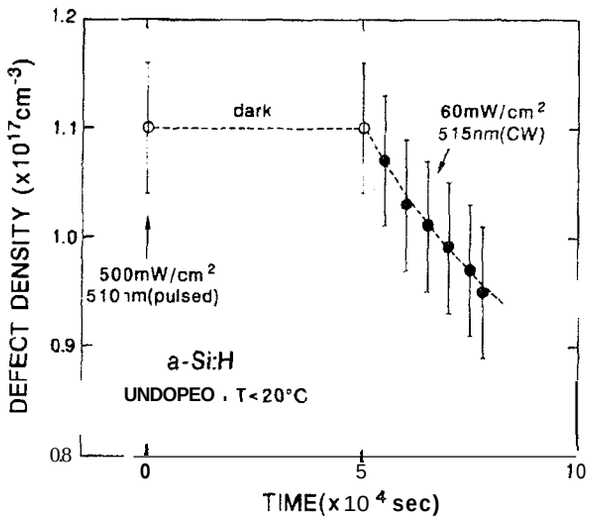

Figure 4: Defect density measured by ESR as a function of time. Open circles correspond to the sample left in the dark at $T < 20°C$ after fabrication, defect creation by pulsed illumination (500 mW cm^{-2}, for 2h). Filled circles show the changes in the spin density of the same sample during subsequent continuous illumination with 60 mW cm^{-2}. The dashed line is a guide to the eye.

Si dangling bond, as seen in Fig. 4. The initial defect density was below $2x10^{16}$ spins cm^{-3}. After 2h of pulsed illumination, the defect density increased to $1.1x10^{17}$ cm^{-3}. The sample was left in the dark for half a day at 20 °C, with no discernible change in the defect density. A decrease of approximately 15% in the defect density was observed when the sample was illuminated with continuous illumination (60 mW cm^{-2}), for 30000s. This result is in good agreement with the photo-conductivity measurements, although the light sources were different in both experiments.

IV. Conclusions

Light-induced annealing of metastable defects in a-Si:H was observed in both, photo-conductivity and ESR, experiments. The experimental data can be reasonably explained by extending the defect creation equation of Stutzmann, Jackson and Tsai[12], adding a simple annealing term proportional to G (generation rate). This result supports the interpretation of defect saturation as an steady state between defect creation and annealing.

Acknowledgements

We would like to thank M. S. Brandt and P. V. Santos for helpful discussions. C. F. O. Graeff acknowledges scholarships from CAPES/DAAD and FAPESP. This work was supported by the Bundesminister für Forschung und Technologie under Contract No. 0328962A.

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