RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Influence of dangling-bond defects on recombination in *a*-Si:H

Helmut Dersch, Andrew Skumanich, and Nabil M. Amer
Applied Physics and Laser Spectroscopy Group, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
(Received 11 February 1985)

Time-resolved photoinduced absorption (PIA) and steady-state photoconductivity (PC) experiments are used to study recombination processes in electron-irradiated hydrogenated amorphous silicon (*a*-Si:H). Defect densities measured by ESR range from $5\times10^{15}/cm^3$ to $10^{18}/cm^3$. It is found that while increasing the dangling-bond density reduces the PC, the PIA decay rate increases. The results are discussed in the context of a recombination model where the defect density determines whether the carriers recombine through a fast bimolecular or a slower monomolecular process.

Recombination processes in *a*-Si:H have been studied extensively using luminescence[1] and photoconductivity[2] experiments. These investigations have shown that the dangling bond is the major recombination center which determines the photoconductivity and luminescence in this material. Seemingly contradictory results were recently obtained by Wake and Amer[3] using time-resolved photoinduced absorption (PIA) measurements which probe the decay of photoexcited carriers. The results in the nanosecond time regime indicate that the PIA decay is slowest in samples with high-defect densities rather than in high-quality, low-defect density material. It has been concluded that in the nanosecond time regime, the properties of the band tail determine the relaxation of excess carriers rather than the dangling-bond defect density.

Since the influence of defects on the recombination properties is usually studied using differently prepared samples, not only the defect density but also the trap density and distribution vary from sample to sample. Furthermore, additional quantities relevant for the recombination process such as the dark Fermi level,[4] optical gap, and microstructure[5] are known to change by varying the deposition parameters which makes it difficult to elucidate the influence of only one of these parameters, namely, the dangling-bond density.

It has been shown recently that the defect density can be changed over three orders of magnitude by electron irradiation and subsequent annealing.[6] This allows the use of the same sample to study the influence of defects on recombination without significantly altering other parameters. In the following, we report on transient PIA and steady-state PC measurements on electron-irradiated *a*-Si:H. The results indicate that two competing processes determine the mechanism by which the photoexcited carriers relax.

Sample preparation, conductivity, and ESR measurements were done at the University of Marburg.[7] Undoped *a*-Si:H samples were prepared by glow-discharge decomposition of 5% SiH_4 diluted in He at a temperature of 280 °C. Samples for conductivity and absorption measurements were typically 1-μm-thick films on quartz substrates. ESR spectra were taken from 10-μm-thick films removed from the substrate (Mo foil). The ESR signal of the as-deposited thick sample is similar to the commonly found dangling-bond resonance with a density of $5\times10^{15}/cm^3$. ESR spectra of thin samples on quartz substrates usually give higher values, which is due to surface and/or interface states and the larger surface-to-volume ratio. This was verified by measuring the spin density of films with various thicknesses (0.4–1.4 μm), from which we deduce a volume defect density of roughly $5\times10^{15}/cm^3$, in agreement with the results found in the thicker sample. The surface or interface spin density amounts to $10^{12}/cm^2$; similar results have been reported by others.[8,9] Electron irradiation was carried out as described in Ref. 6 and leads to an increase in spin density to more than $10^{18}/cm^3$ without changing the line shape and g value of the ESR signal. This could be measured only in the thick sample since electron irradiation creates a strong background signal in the quartz substrates of the thin-film samples. The spin density N_s is reduced by annealing the samples at increasingly higher temperatures T_A (annealing time 30 min), and N_s is restored to its original value after a 220 °C anneal. The conductivity was measured between two evaporated Cr contacts. In the case of the photoconductivity studies, σ_{ph} was measured with white light from a tungsten-halogen lamp (50 mW/cm^2) followed by an edge filter which transmits photons with energies above 1.45 eV.

Time-resolved photoinduced absorption was measured in the time regime of 10 nsec to 1 μsec using a 10-Hz Nd-YAG-pumped dye laser with 4-nsec pulses of 2.2-eV photons, and a cw broadband (0.9–1.45 eV) ir probe beam. Details of the setup have been described elsewhere,[3] and the temperature range at which data were taken was 120–200 K.

Finally, the optical absorption was measured using the photothermal deflection scheme described in Ref. 10.

In Fig. 1, conductivity and ESR results are shown as a function of the spin density. The dark conductivity was measured between T_A and 0 °C and shows an activated behavior. Although a slight increase in both the activation energy E_a and the prefactor σ_0, with decreasing N_s, can be observed, the overall dependence of these quantities on the defect density is rather weak. Much larger changes are observed when differently prepared samples are used. According to Spear, Allan, LeComber, and Gaith,[4] E_a can vary in undoped samples between 0.6 and 0.9 eV with σ_0 spanning almost five orders of magnitude. The constant activation energy, as observed in the irradiated sample, implies that the dark Fermi level E_F remains almost constant over the entire defect density range. This is an important premise for the present study, since it is known that the recombination properties of *a*-Si:H depend strongly on the position of E_F.[2]

In contrast to σ_d, the photoconductivity changes by nearly three orders of magnitude, which is roughly the change in defect density. Since the mobility, μ, enters both the pre-

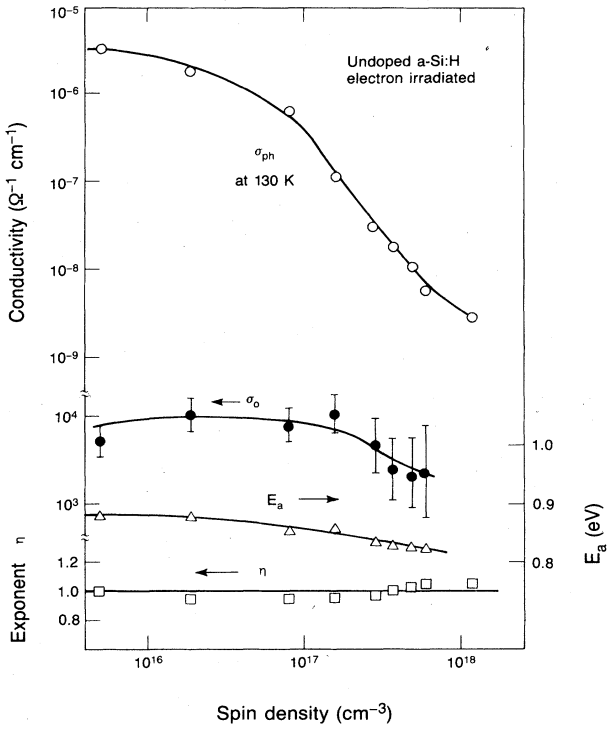

FIG. 1. Transport properties of electron-irradiated *a*-Si:H at various annealing stages as a function of the spin density. Shown is the activation energy E_a and prefactor σ_0 of the dark conductivity, the photoconductivity σ_{ph} at $T=130$ K, and the exponent η in the relation $\sigma_{ph} \propto I^{\eta}$ (I, light intensity).

factor σ_0 of the dark conductivity and the photoconductivity, we conclude that the much larger change in the case of σ_{ph} is mainly caused by a reduction of the carrier lifetime due to the increased defect density rather than by changes in μ. However, we do not observe a simple $1/N_s$ dependence, rather a weaker decay for $N_s < 10^{17}/\text{cm}^3$ and a stronger one for $N_s > 10^{17}/\text{cm}^3$. Moreover, the sharpness of this transition is temperature dependent, becoming more pronounced above, and weaker below $T=130$ K as depicted in Fig. 1. The intensity dependence of σ_{ph} was measured in the range 0.2–80 mW/cm^2 using neutral density filters. The exponent η in the relation $\sigma_{ph} \sim 1^{\eta}$ indicates momomolecular recombination kinetics for all defect densities.

Figure 2 compares optical absorption spectra from an unirradiated and irradiated sample. The spectrum consists of the typically reported features, namely, an exponential edge ascribed to transitions involving tail states (Urbach edge) and a low-energy band due to transitions from deep centers, predominantly dangling bonds.[10] Electron irradiation influences only the latter one, whereas the Urbach edge (slope 65 meV) remains unaffected. The defect absorption band increases upon irradiation without changing its shape. Therefore, we can conclude, that all changes introduced by electron irradiation are confined to deep gap states, while the band edges and tails remain unaffected. This provides additional support for the suitability of the present samples to study the influence of the defect density on recombination properties. The increase in defect density, however, amounts to only a factor of 10 and is smaller than observed in ESR. The difference is mainly due to two effects: First,

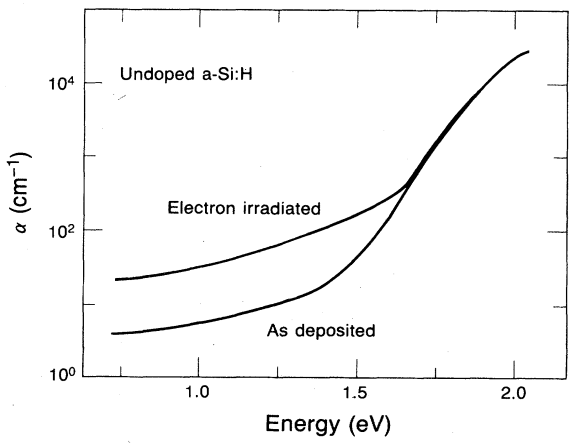

FIG. 2. Optical absorption spectra of irradiated and unirradiated *a*-Si:H.

the absorption of the unirradiated sample is affected by surface and interface states similar to the ESR data described above and appears to be higher than the volume absorption. Second, the irradiation-induced defects begin to anneal even at room or slightly higher temperatures.[6] Since the optical measurements were performed several weeks after the ESR measurements, a noticeable part of the defects may have been already annealed. Following a procedure described in Ref. 9 we roughly estimate the defect density of the irradiated sample from the absorption spectrum to be $4\times10^{17}/\text{cm}^3$. Unlike ESR, the optical absorption detects all gap states irrespective of their spin properties.

Figure 3 shows PIA decay data for various excitation densities η_{exc} measured on an unirradiated and irradiated sample. Similar transients have been obtained on a second set of samples. At low intensities ($\eta_{exc} < 5\times10^{17}/\text{cm}^3$) the data can be approximated by a straight line which corresponds to a power-law decay ($\Delta T/T \propto t^{-\alpha}$) with $\alpha=0.15$. In both samples the decay becomes faster at higher intensities and shows deviations from the power-law behavior. In contrast to what one might expect the fast decay component is most prominent in the unirradiated, low-defect density sample. This can be more clearly seen in Fig. 4, where the slope α of the transients at 20 nsec and 2 μsec is plotted as a function of η_{exc}. At long times and low-excitation densities α approaches a constant value of 0.15 which is roughly the same for both defect densities. Multiple trapping (MT) theory[11] predicts a value given by the temperature and the exponential slope, E_0, of the trap distribution:

$$\alpha = \frac{kT}{E_0} \quad . \tag{1}$$

Assuming that the slope of the Urbach edge (Fig. 2) reflects the trap density of states, we obtain $\alpha=0.15$ in agreement with the low-excitation-density data. Also, the temperature dependence given by Eq. (1) was verified in the range 120–200 K which supports the multiple trapping model as being adequate to describe the transients for low η_{exc}.

With increasing intensity α becomes larger, reaching 0.33 in the as-deposited and 0.27 in the irradiated sample. The intensity-dependent decay constant requires a second bimolecular or higher-order process to be present. The transition between the monomolecular and bimolecular regions occurs at roughly $5\times10^{17}/\text{cm}^3$. Similar transitions at the

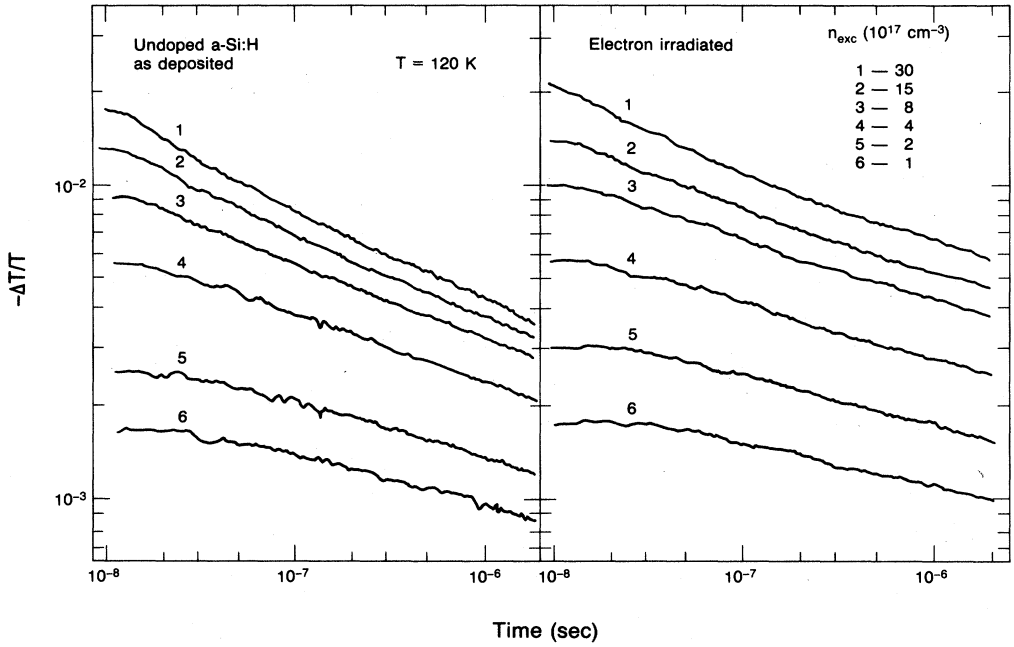

FIG. 3. Decay of photoinduced sub-band-gap absorption in irradiated and unirradiated a-Si:H for various excitation densities η_{exc}.

same excitation density have been observed in luminescence decay experiments. It has been suggested that the fast process is due to Auger recombination[1,12] or nongeminate, bimolecular recombination[1] of band tail carriers. The present results clearly show that the fast component decreases as the defect density is enhanced, whereas the monomolecular decay at low-excitation densities remains almost unaffected.

From the photoconductivity results we conclude that the steady-state recombination in the present samples is dominated by a monomolecular process involving the dangling-bond defects. It is therefore most likely that the same process governs the monomolecular PIA decay at low excitation densities. Tauc[13] concluded from the spectral dependence of the photoinduced absorption band that it is mainly due to holes trapped in the exponential valence band tail. The process responsible for the PIA decay is therefore a transition between a trapped hole and the defect, and has been successfully described within the multiple trapping model.[3,10]

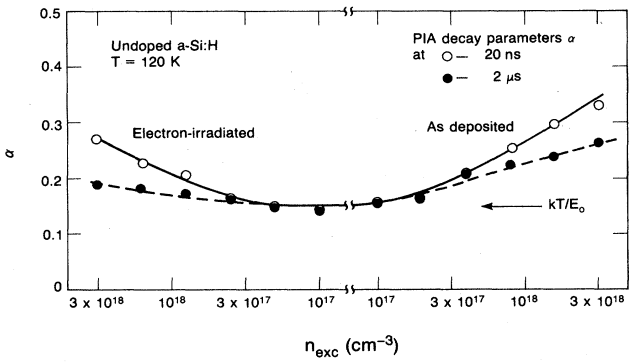

FIG. 4. Slope of the transients of Fig. 3 at 20 ns and 2 μs as a function of the excitation density.

MT theory predicts a power-law decay at long times with a decay parameter α determined only by the shape of the trap density of states and temperature, but independent of the defect density. This has been verified by Wake and Amer[3] who indeed found a correlation between α and E_0. As has been demonstrated above, the present data support the multiple trapping model in the regime of small η_{exc}. It should be noted that according to MT theory the defect density will influence the transient and eventually govern the steady-state recombination, the latter being observed in the photoconductivity experiment. The influence on the transient, however, is confined to the onset, τ, of the power-law decay which will decrease inversely as the number of recombination centers; whereas the decay parameter α itself is independent of N_s. This should lead to a vertical offset between transients from samples with different defect densities which is, however, not observed. We believe this to be a consequence of the competing fast recombination channel which masks the influence of different onsets, τ, of the dangling-bond recombination.

The decay at high-excitation densities is ascribed to recombination between band tail carriers which may occur through a direct bimolecular process or, involving a third carrier, through Auger recombination. The unexpected inverse dependence of this process on the defect density can be understood within a recombination model recently derived from spin-dependent photoconductivity measurements.[6] According to that model, recombination at dangling bonds occurs by tunneling of trapped electrons towards neutral dangling bonds thereby forming a doubly occupied, negatively charged defect state. Recombination is completed by subsequent transitions between trapped holes and the negatively charged dangling bond. This latter process is responsible for the decay of the PIA at low intensities and long times, and can be accounted for by the multiple trapping model. At higher carrier densities, a second recombination

mechanism becomes operative which depends on both hole and electron densities. Due to the low-defect density, more electrons will remain in the conduction band tail of the unirradiated sample than in the case of the irradiated one, where a larger fraction of electrons has been captured by the defects. Therefore, the bimolecular recombination channel will be stronger in the unirradiated sample as is clearly observed. In the irradiated sample the fast capture of electrons by dangling bonds forces more carriers into the slower defect-related recombination channel and makes them unavailable for the bimolecular process. This explains the slower decay of the hole population as observed in the PIA experiment.

We have shown that two recombination mechanisms account for the decay of the photoinduced absorption. At low excitation, slow decay dominates the transient and can be described by recombination of trapped holes via charged defect states within a multiple trapping model. At high intensites, a bimolecular process is observed which is most pronounced in low-defect-density samples. This can be explained qualitatively within a recombination model where the defect density determines the fraction of carriers which recombine in a bimolecular or monomolecular process.

One of the authors (H.D.) gratefully acknowledges a grant from the Deutsche Forschungsgemeinschaft. Another (A.S.) gratefully acknowledges support by the Hertz Foundation. This work was supported in part by the Director, Office of Energy Research, Physical and Technological Research Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1]R. A. Street, Adv. Phys. **30**, 593 (1981).

[2]W. E. Spear and P. G. LeComber, in *Photoconductivity and Related Phenomena,* edited by J. Mort and D. M. Pai (Elsevier, New York, 1976), p. 213.

[3]D. Wake and N. Amer, Phys. Rev. B **27**, 2598 (1983); D. Wake, Ph.D. thesis, University of California, Berkeley, 1983 (unpublished).

[4]W. E. Spear, D. Allan, P. G. LeComber, and A. Gaith, Philos. Mag. B **41**, 419 (1980).

[5]H. Fritzsche, Sol. Energy Mater. **3**, 447 (1980).

[6]H. Dersch, L. Schweitzer, and J. Stuke, Phys. Rev. B **28**, 4678 (1983).

[7]H. Dersch, Ph.D. thesis, University of Marburg, Marburg 1983 (unpublished).

[8]J. C. Knights, J. Biegelsen, and I. Solomon, Solid State Commun. **22**, 133 (1977).

[9]S. Hasegawa and Y. Imai, Philos. Mag. B **46**, 239 (1982).

[10]W. Jackson and N. Amer, Phys. Rev. B **25**, 5559 (1982).

[11]J. Orenstein and M. Kastner, Solid State Commun. **40**, 85 (1981).

[12]W. Rehm and R. Fischer, Phys. Status Solidi (b) **94**, 595 (1979).

[13]J. Tauc, in *Festkörperprobleme, Advances in Solid State Physics,* edited by P. Gross (Vieweg, Braunschweig, 1982), Vol. XXII, p. 85; P. O'Connor and J. Tauc, Phys. Rev. B **25**, 2748 (1982).