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The influence of microstructure on x-ray-induced degradation of dark conductivity of a-Si:H layers

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Abstract. X-ray-induced degradation of dark conductivity at 293 K characterized by the relation between the values before and after the exposure S was investigated in magnetron-sputtered a-Si:H layers. A variation in the incorporation of hydrogen in these layers described by the relation of the integrals of the IR absorption peaks at 2000 cm^{-1} and 2090 cm^{-1} was carried out by a deposition of the layers at various substrate temperatures and argon partial pressures. We found a direct correlation between the hydrogenated void fraction R and the degradation factor S and an influence of the initial dangling bond density measured with the constant-photocurrent method (CPM) on the degradation factor. Some mechanisms of defect generation are discussed as sources of the x-ray-induced degradation behaviour of the dark conductivity.

1. Introduction

Devices based on a-Si:H layers are widely used as the base for x-ray detectors, especially in medicine. An advantage of a-Si:H layers is the high deposition rates, allowing deposition of large areas [1].

Degradation effects in the behaviour of the dark conductivity and the photoconductivity occur in a-Si:H layers [2].

Two groups of samples must be distinguished with regard to the degradation of the dark conductivity. The dark conductivity decreases in samples of the first group and increases in samples of the second group after irradiation. These changes anneal at temperatures around 180 °C. Furthermore the x-ray exposure causes a decrease in the photoconductivity and an increase in the density of states of the dangling bonds (DBs) determined with the constant-photocurrent method [2].

The behaviour of samples of group 1 are comparable with the Staebler–Wronski effect (SWE) after exposure to light [3]. Otherwise the behaviour of samples of group 2 shows similarities with the abnormal SWE described in [4] and with the behaviour of a-Si:H layers after gamma-ray exposure [5]. In this paper we will investigate some aspects of the cause of this behaviour. We will show the importance of the incorporation of the hydrogen and of the structure of the layers. Similarities to the SWE can be noticed.

2. Experimental details

The a-Si:H layers were produced by DC magnetron sputtering (MSP). The equipment allows the deposition of six different groups of layers within one sputter cycle. One group of

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samples consists of one layer on c-Si substrate for IR measurement and two layers on Corning glass substrates for NIR spectroscopy and for electrical measurements.

The sputtering power and the hydrogen partial pressure were held constant at 200 W and 0.3 Pa, respectively. The distance between the target and the substrate was 55 mm. The argon partial pressure and the substrate temperature were varied. A thickness of the layers in the range of 0.6–1.5 μm was used.

Electrical measurements were performed on evaporated aluminium contacts, which were arranged coplanarly. The following measuring cycles were used to determine the degradation effects.

(i) The samples were heat treated at 200 °C for 1 h (state G).

(ii) Then the samples were irradiated for 2 h and the dark conductivity was measured after this in the temperature range 30–50 °C (state I).

(iii) Finally the samples were heat treated at 200 °C again for 1 h (state A).

The dark conductivity was measured in all cases during the cooling process. The cooling rate was 0.6 K min^{-1} in the case of states G and A and 1.0 K min^{-1} in the case of state I. The relation S between the dark conductivity after (σ_I) and before (σ_G) the irradiation ($S = (\sigma_I(293\ \mathrm{K})/(\sigma_G(293\ \mathrm{K}))$ was used as a parameter for the characterization of the degradation of the dark conductivity.

Infrared measurements were performed with a double-beam spectrometer at room temperature. The samples consisted of a c-Si substrate (250 μm thick) and the a-Si:H layer (0.6–1.5 μm thick).

The hydrogen stretching mode between 1800 and 2300 cm^{-1} was investigated. In this region appear two absorption peaks: the stretching mode of the hydrogen monohydrides at 2000 cm^{-1} and the stretching mode of the hydrogen dihydrides and of hydrogen clusters at inner interfaces in microvoids at 2090 cm^{-1} as described in [6] and [7]. This absorption band was separated into individual absorption peaks. The relation R was calculated after Yoon [8] ($R = I_{2090}/(I_{2090} + I_{2000})$, with I_{2090} and I_{2000} the integrals of the absorption peaks at 2090 cm^{-1} and 2000 cm^{-1}, respectively).

The factor R describes the fraction of the hydrogenated microvoids on the bonded hydrogen in the a-Si:H layer. This can be concluded from the investigations of Mahan *et al* [6]. They found a correlation between the integral of the absorption peak at 2070 cm^{-1} and the microvoid volume fraction determined by small-angle x-ray scattering. Danesh *et al* [9] found also a connection between this factor R and the micropore density detected by field-assisted ion exchange.

X-ray-induced changes in the subgap absorption region were determined with the aid of the constant-photocurrent method (CPM) (see also [2]). The absorption coefficient in the region of weak absorption ($E_{ph} = 1.2$ eV) is directly proportional to the density of states of the dangling bonds [10]. We use the absorption coefficient $\alpha(1.2\ \mathrm{eV})$ as a relative value of the density of neutral DB states because of the difficulties in the calculation of the density of DB states from CPM spectra in undoped a-Si:H layers (see, e.g., [10]).

An x-ray tube with a copper anode was used as x-ray source. The applied voltage was 40 kV. An ion dose rate of 1.3 A kg^{-1} was measured within the plane of the sample with the aid of a calibrated dosimeter for soft x-rays.

In some cases differences occur between the values of the dark conductivity and the absorption coefficient at 1.2 eV before the exposure and after the annealing of samples of both groups (compare the states G and A in figure 2 and in table 1). There are two reasons for this behaviour.

(i) Changes in these parameters are caused by the x-ray exposure as well as by heat treatment up to 200 °C. Therefore, during the annealing not only x-ray-induced changes were annealed but also additional defects were generated or destroyed.

(ii) Otherwise defects created by x-ray exposure were not annealed completely.

In all cases the x-ray-induced changes were significantly higher than the differences between the values of the initial and annealed states.

Measurements within the initial state were reproducible within an error limit of 20%.

3. Results and discussion

The dependences of the parameter R and the x-ray-induced degradation described by the parameter S on the sputtering conditions such as argon pressure and the substrate temperature were investigated.

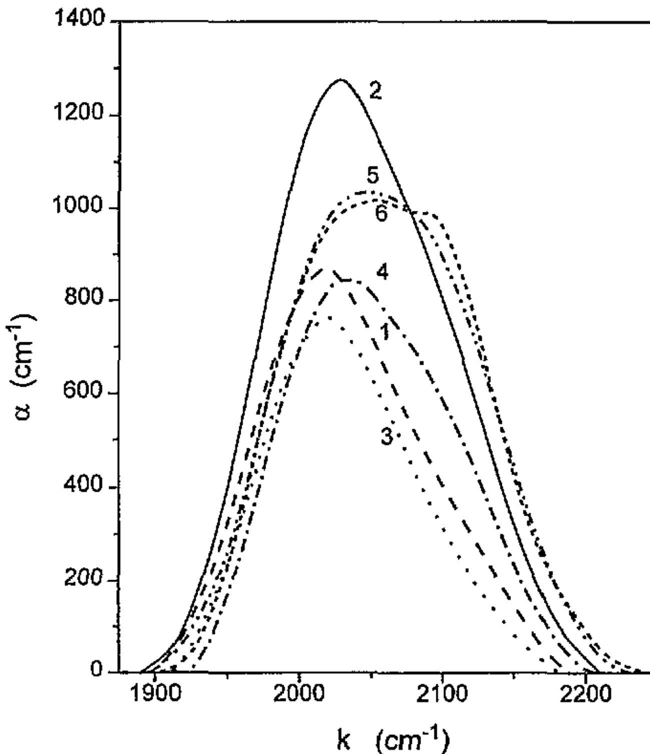

Figure 1. Infrared absorption spectra in the range of the stretching mode of a-Si:H layers deposited at various substrate temperatures. The sputtering parameters were p_{H2} = 0.3 Pa; p_{Ar} = 0.6 Pa; P_{sp} = 200 W (curve numbers: 1, 260 °C; 2, 230 °C; 3, 200 °C; 4, 170 °C; 5, 140 °C; 6, 130 °C).

Infrared spectra in the region of the stretching mode from 1900 to 2300 cm^{-1} are shown in figure 1 for samples produced at various substrate temperatures. The peak at 2090 cm^{-1} decreases with increasing substrate temperatures. Therefore, as shown in figure 3, the factor R decreases. Rüther *et al* [11] also obtained similar results in RF-sputtered a-Si:H layers. The degradation behaviour of the a-Si:H layers also depends on the substrate temperature. Figure 2 shows the dark conductivity before and after the irradiation and after the annealing of two samples deposited at different temperatures. The dark conductivity increases at

a low substrate temperature (sample 2) and decreases at high substrate temperature after irradiation. This behaviour, described by the factor S, is also shown in figure 3. Both parameters decrease with increasing substrate temperatures. Above 230 °C the factor S is lower than unity.

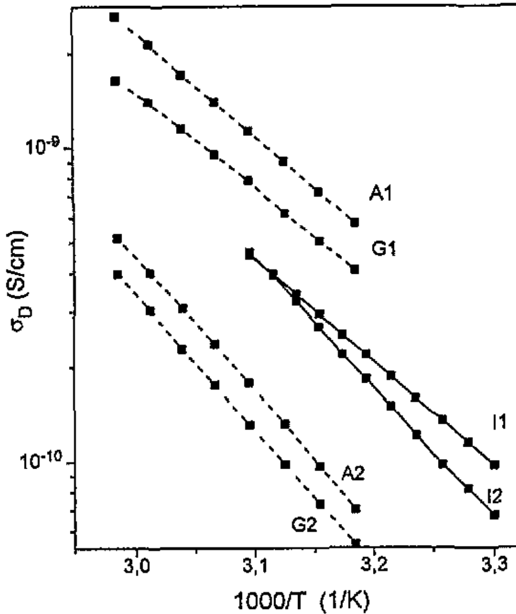

Figure 2. The temperature-dependent dark conductivity of two samples deposited at two different substrate temperatures at various states (G, initial state; I, irradiated state; A, annealed state; curve numbers: 1, 260 °C; 2, 200 °C).

Table 1. Absorption coefficient α(1.2 eV) and Urbach energy E_U, determined with the CPM, of two different samples with different values of the structural parameter R and the degradation parameter S in different states (G, initial state; I, irradiated state). The hydrogen content was 8–9 × 10^{21} cm^{-3}.

Parameter	State	Sample 1	Sample 2
R		0.35	0.44
S		0.03	3.4
E_U (eV)	G	60.8	69.2
α(1.24 eV) (cm^{-1})	G	0.83	7.4
α(1.24 eV) (cm^{-1})	I	3.18	20.9

Furthermore, the factor R also decreases with increasing argon partial pressure (figure 4) and reaches a minimum at a pressure of 0.7 Pa. The degradation factor S shows the same behaviour as is seen in figure 4.

It can be noticed that the degradation factor S and the factor R show an equivalent dependence on the sputtering parameters. Therefore, we conclude that the degradation of the dark conductivity is primarily influenced by the hydrogenated void fraction R. Bhattacharya and Mahan [12] also show a similar dependence of light-induced changes of the density of generated states on the factor R. Ohagi *et al* [13] found an increase of the light-induced degradation of the photocurrent with increasing substrate temperature. Here the variation of the substrate temperature corresponds to changes in the structural properties.

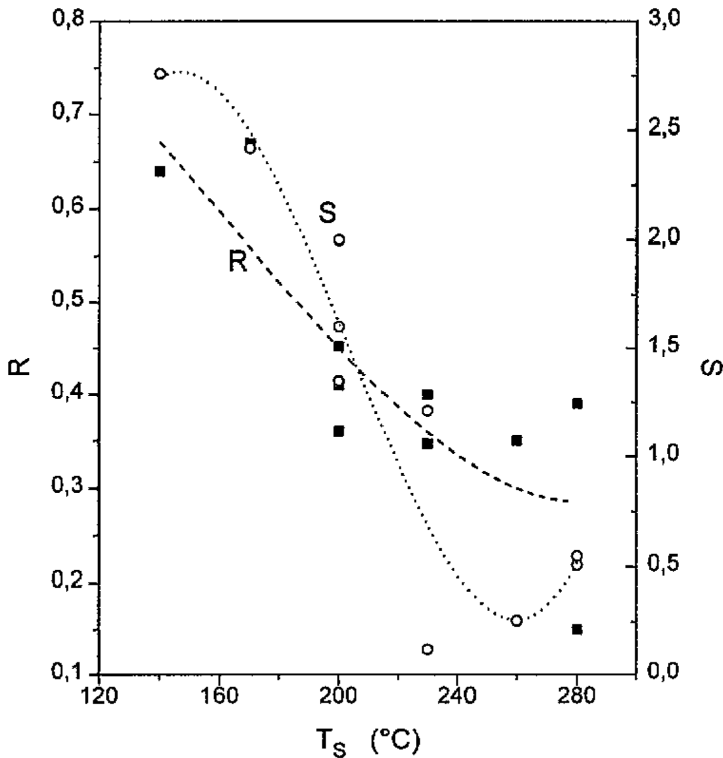

Figure 3. Hydrogenated void fraction R and degradation factor S in dependence on the substrate temperature. Sputtering conditions were $p_{H2} = 0.3$ Pa, $p_{Ar} = 0.6$ Pa.

The conclusion of our investigations is a correlation between the fraction of the hydrogenated voids R and the x-ray-induced degradation factor S. This is shown in figure 5. The degradation factor S changes its behaviour from $S > 1$ (the dark conductivity increases after the irradiation) to $S < 1$ (the dark conductivity decreases after the irradiation) within the interval of R from 0.3 to 0.4.

Thus we distinguished two groups of samples corresponding to different values of the degradation factor S (see also [2]). Samples of group 1 show $S < 1$ and samples of group 2 show $S > 1$.

The samples of the two groups show different initial parameters (see table 1). Group 1 (sample 1) exhibits an essential lower absorption coefficient in the region of the neutral DB at 1.2 eV compared with samples of group 2 (sample 2). Taking into account a calibration factor of 2.4×10^{16} cm^3 for a value of $\alpha(1.2 \text{ eV}) = 1$ cm^{-1} (according to [10]) in sample 1 the DB density is 2×10^{16} cm^{-3} and in sample 2 it is 2×10^{17} cm^{-3}. In samples of both groups the DB absorption coefficient at 1.2 eV increases after the x-ray exposure.

The initial Urbach energy changes significantly in dependence on the factor R (see table 1). The Urbach energy is lower in samples of group 1 than in samples of group 2. Such a dependence was also obtained by Mahan *et al* [14].

All this behaviour can be explained by some mechanism of the creation of defects.

(i) The x-ray irradiation causes a direct bond breaking of weak Si–Si bonds and produces a generation of additional DB states, according to investigations by Saito and Yoshida [15] using UV irradiation and Schneider and Schröder [16] using 20 keV electron radiation. The x-ray photon energy of 10–40 keV used can produce photoelectrons with energies between 8 and 38 keV with respect to an absorption of electrons in the K shell (binding energy,

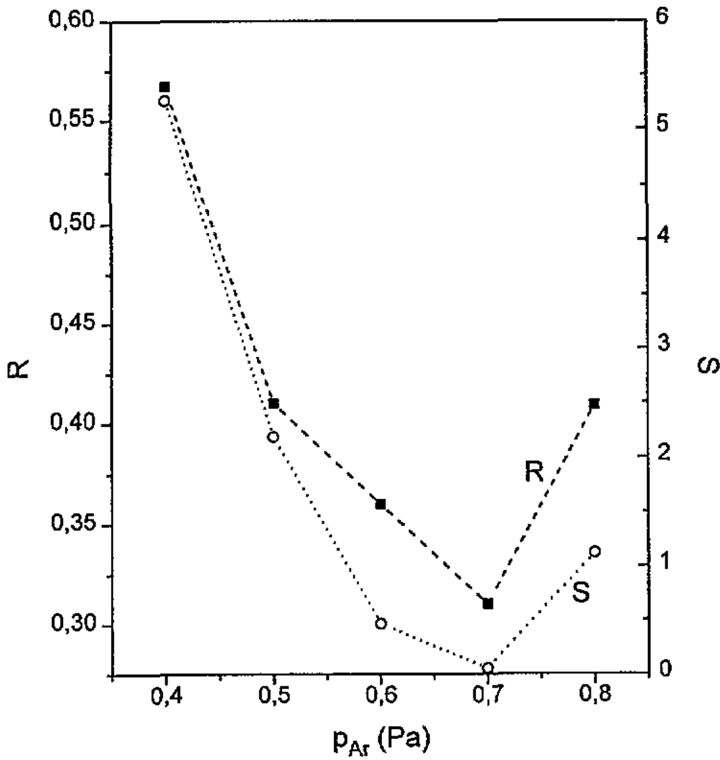

Figure 4. Hydrogenated void fraction R and degradation factor S in dependence on the argon partial pressure. Sputtering conditions were $p_{H2} = 0.3$ Pa, $T_s = 200\,^{\circ}$C.

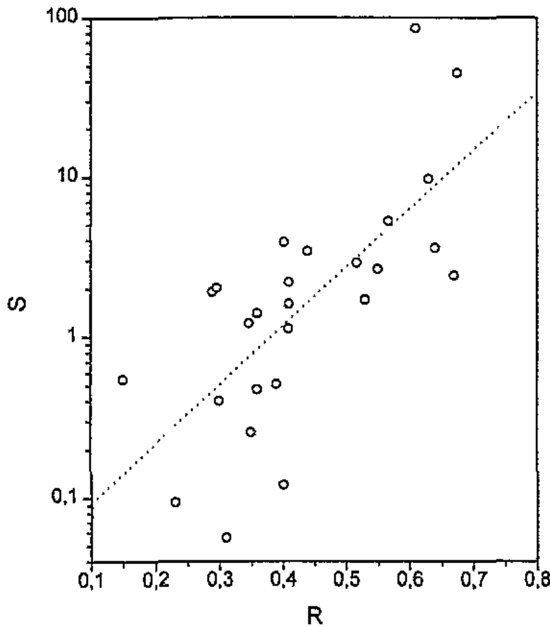

Figure 5. Degradation factor S in dependence on the hydrogenated void fraction R for various a-Si:H layers.

1.8 keV). Thus not only Si–Si bonds were broken but also Si–H bonds with binding energies of 3.6 eV [16].

This is the main process to explain the x-ray-induced behaviour of the dark conductivity in samples of group 1. In consequence of this DB defect creation the Fermi level shifts towards the middle of the mobility gap and the dark conductivity decreases, induced by the x-ray exposure.

(ii) One possible mechanism to explain the behaviour of samples of group 2 is the creation of charged DB states such as D^- or D^+ centres or recharging of D^0 to D^- or D^+. Such a mechanism was found by Imagawa *et al* [5] in a-Si:H layers irradiated with gamma-rays. Thus the Fermi level shifts to the edges of the mobility gap and the dark conductivity increases after the x-ray exposure.

(iii) Otherwise an x-ray-induced creation of impurity complexes (especially O-related defects) as observed by Pontuschka *et al* [17] at low temperatures of 77 K or a creation of intrinsic tail states can take place. In this case these complexes would act as a dopant and the density of tail states would increase after the irradiation, so the Fermi level would shift towards the edges of the gap and the dark conductivity increase.

The whole mechanism must be influenced or controlled by the microstructure and the initial DB density of the a-Si:H layers. Such a correlation of defect generation with the factor R is well known through investigations of light-induced degradation by Bhattacharya and Mahan [12] and Yoon [8].

An x-ray-induced diffusion of hydrogen cannot be assumed as the cause of the behaviour of samples of both groups, because no irradiation-induced hydrogen diffusion has been observed at room temperature from the literature.

These behaviours can be explained by an assumption of charged DB states in a-Si:H layers correspondingly deduced from investigations of the SWE. For example Irrera [18] shows that a-Si:H layers contain beside the neutral also charged DB states. Zellama *et al* [19] assume the existence of a $T_3^+-T_3^-$ pair centre in addition to neutral DB states D^0 in a-Si:H layers. Each part of the pair centre captures charge carriers and converts either to a D^0 state or to the other charge state. These trap processes depend on the distance of the pair centre from unstrained or strained regions [19].

Thus, the Fermi level shifts towards the valence or conduction band tail during the irradiation in dependence on the trap process.

The microstructure influences especially the strain regions in the a-Si:H layer and therefore the trap process [19]. Furthermore Yokomichi and Morigaki [20] found an influence of internal surface (e.g. microvoids) on the structure of the DB states by investigations with ENDOR.

The assumption of the creation of charged DB states coincides with results of investigations by Imagawa *et al* [5]. They obtained an increase of D^+ states (i.e. a conversion to p-type conductivity) and no noticeable increase in the D^0 states after the gamma-ray irradiation.

We assume that there is a greater influence of charged DB states on the degradation effects induced by irradiation with photons with higher energy (e.g. UV, x-rays or gamma-rays) than with light irradiation, because the radiation breaks directly all Si–Si bonds (not only the weak Si–Si bonds). Therefore the x-ray-induced effects should be greater than light-induced effects.

In summary, magnetron-sputtered a-Si:H layers deposited under various conditions were investigated with respect to x-ray-induced degradation of dark conductivity. The dark conductivity decreases or increases in samples with low or high values of the hydrogenated void fraction R and initial density of DB states, respectively. The existence of charged DB states and different trapping processes depending on the microstructure is assumed as the cause of the experimental results.

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