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The nanostructural analysis of hydrogenated silicon films based on positron annihilation studies

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A B S T R A C T

Due to the complex nature of hydrogenated amorphous and microcrystalline silicon (a-Si:H; μc-Si:H) a profound understanding of the Si:H nanostructure and its relation to the Staebler–Wronski effect (SWE) is still lacking. In order to gain more insight into the nanostructure we present a detailed study on a set of Si:H samples with a wide variety of nanostructural properties, including dense up to porous films and amorphous up to highly crystalline films, using Doppler broadening positron annihilation spectroscopy (DB-PAS) and Fourier Transform infrared (FTIR) spectroscopy. The results obtained from these material characterisation techniques show that they are powerful complementary methods in the analysis of the Si:H nanostructure. Both techniques indicate that the dominant type of open volume deficiency in device grade a-Si:H seems to be the divacancy, which is in line with earlier positron annihilation lifetime spectroscopy (PALS), Doppler broadening (DB) PAS and FTIR studies.

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1. Introduction

The complex nature of hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) is the main reason why there are still large ambiguities associated with the understanding of the nanostructure of Si:H. As a result, there is still no consensus on the mechanism behind the reversible changes in electrical properties of a-Si:H under light exposure, also known as the Staebler–Wronski effect (SWE) [1]. This is why an improved understanding of the Si:H nanostructure is particularly important. Therefore, in this contribution we present a detailed study on a set of Si:H samples with a wide variety of nanostructural properties including dense up to porous films and amorphous up to highly crystalline films. To gain more insight into the Si:H nanostructure we use a combination of positron annihilation spectroscopy (PAS) [2–6] and Fourier Transform infrared (FTIR) spectroscopy [7–9].

In Doppler broadening (DB) PAS the S parameter is a measure for the size of the dominant open volume deficiency [4,5,10]. The nanostructure parameter K, which can be deduced from FTIR analysis, is defined as the number of hydrogen atoms in the volume of a missing Si atom and indicates the dominant type of hydrogenated vacancy [7,9]. In this work it is shown that the S parameter correlates strongly with the found nanostructure parameter K. The dominant type of open volume deficiency in device grade a-Si:H seems to be the divacancy, which is in line with earlier observations from positron annihilation lifetime spectroscopy (PALS) [4], DB-PAS [3,5] and FTIR [9] studies. This result further underlines the important role of hydrogenated divacancies in a-Si:H, which has recently been illustrated in detail [9].

2. Experimental details

2.1. Deposition of films

A series of Si:H films is deposited either on Corning Eagle 2000 (EA) or XG type glass substrates and all films are also deposited on crystalline silicon (c-Si) substrates for FTIR characterisation. The used deposition methods are radio frequency plasma-enhanced chemical vapourdeposition (rf-PECVD) and expanding thermal plasma chemical vapour deposition (ETPCVD). This enables the possibility of studying the dependence of the deposition method on the nanostructure. All Si:H samples listed in Table 1 are intrinsic. The amorphous films are all deposited from pure silane (SiH_4), whereas the microcrystalline films are deposited from hydrogen-diluted silane ($R=[H_2]/[SiH_4]$). The a-Si:H samples are deposited at different rf power densities (P_{rf}), since this influences the nanostructure significantly without inducing a phase transition in the material. Similarly, different rf powers are used to deposit the μc-Si:H films. It should be clear that the samples are selected based on a wide variation in nanostructure. Note that the listed thicknesses (d) are determined from Reflectance / Transmittance (RT) measurements.

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Table 1
Deposition conditions and film thicknesses for samples with a wide variation in nanostructure. Samples a1–a6 correspond to amorphous samples; μc1–μc2 represent microcrystalline films.

#	CVD type	d [nm]	R_d [nm/min]	P_{rf} [W/cm^2]	p [mbar]	T_{sub} [°C]	R [–]
a1	rf-PE	276	9.9	0.024	0.7	180	0
a2	rf-PE	498	12.5	0.035	1	160	0
a3	rf-PE	639	21.0	0.049	1	160	0
a4	rf-PE	564	28.2	0.069	1	160	0
a5	ETP	391	21.7	–	0.15	350	–
a6	ETP	417	92.7	–	0.62	350	–
μc1	rf-PE	160	4.9	0.097	2	180	60
μc2	rf-PE	646	21.5	0.556	9	180	63

2.2. Characterisation of films

DB-PAS is performed using the positron depth profiling method [10] to study vacancies in Si:H films deposited on Corning glass. A variable energy positron beam with an intensity of 10^5 e^+/s and a diameter of 8 mm is obtained via moderation of positrons emitted from a ^{22}Na source through a tungsten foil. The annihilation radiation is measured at room temperature by a germanium solid state detector with a resolution of 1.4 keV as the Doppler-broadened 511 keV γ-ray photopeak characteristic of 2γ annihilation of electron-positron pairs. A total of 5×10^5 counts are collected under the γ-ray photopeak for each of the selected positron implantation energies ($E_{positron}$) in the range of 0.25–25 keV.

FTIR spectroscopy is conducted to analyse the Si:H films deposited on c-Si substrates using a Thermo Fisher Nicolet 5700 FTIR spectrometer in transmittance mode.

3. Results

In DB-PAS two parameters are conventionally used to characterise the spectrum of the annihilation radiation: S and W. These two Doppler broadening parameters are calculated as the ratio of the counts in the central and wing parts of the Doppler-broadened 511 keV photopeak to the total peak count [10], respectively. Physically, S can be understood to represent annihilation events with low momentum electrons (small energy shift from 511 keV) which are the valence electrons of atoms in the sample under investigation. Similarly, W corresponds to annihilation events with high momentum electrons (larger energy shift from 511 keV) which are the core electrons of atoms in the sample. As an example, the positron Doppler broadening depth profiles of samples a1 and a4 (see Table 1) are shown in Fig. 1.

Generally, three regions can be identified in the depth profiles shown in Fig. 1a: a fairly constant S value in the low energy range (1–5 keV) that represents the Si:H film and decreasing S values for positron energies below (<1 keV) and above (>5 keV) this region due to positron annihilation at the surface and in the substrate respectively. It is clear from the measurement data in Fig. 1a and c that both S and W as well as the Si:H film thicknesses for samples a1 and a4 are substantially different. In order to extract the S and W values both the S(E) and W(E) depth profiles are fitted using the VEPFIT program [11] assuming a two-layer structure (Si:H film / Corning glass) with constant S and W values for each layer. The depth profiles in Fig. 1a and c are fitted by solving the second order differential equation that describes the positron diffusion process in the sample. A Makhovian implantation profile is used with a mean implantation depth $\bar{z}=AE^n/\rho$, where E is the positron implantation energy in keV and the parameters n = 1.62 and $A=4.0\ \mu g\ cm^{-2} keV^{-1.62}$ [10]. A density of $\rho=2.3\ g\,cm^{-3}$ is assumed for the Si:H films. The results of the fitting procedure are shown as the solid and dashed lines in Fig. 1a and c. This fitting procedure is conducted to finally obtain values for S and W of the Si:H film and the glass substrate; an example of the calculated S values for both the film and the substrate as well as the thickness of the film is given in Fig. 1b. It seems from Fig. 1d

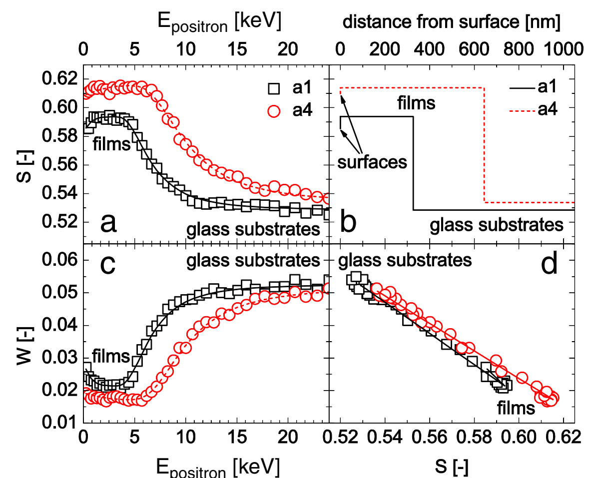

Fig. 1. DB-PAS depth profiles of samples with different thicknesses (a1 and a4) showing (a) S parameter, (b) result of VEPFIT analysis using $S(E_{positron})$ as input, (c) W parameter, and (d) S–W diagram with $E_{positron}$ as running parameter.

that both films shown here have a homogeneous composition, since the (S,W) coordinates corresponding to the surface, the bulk of the Si:H film, and the glass substrate closely approximate a straight line in the S–W diagram.

All samples listed in Table 1 are analysed using DB-PAS and VEPFIT to obtain the (S,W) coordinate for each Si:H film. The thus obtained (S,W) values can be used to observe trends in the data, but do notenable a direct comparison with previously reported (S,W) values in the literature. This is due to the fact that the absolute (S,W) valuesdepend on the overall instrument resolution of the Doppler broadening setup and the momentum ranges applied in the determination of S and W. In order to enable a better comparison with previously reported data, all (S,W) values are normalised to the (S,W) coordinate of c-Si, which is characterised individually by DB-PAS for this purpose ($S_{c\text{-}Si}=0.5744\pm0.0002$, $W_{c\text{-}Si}=0.0265\pm0.0002$). The normalised (S,W) coordinates of the various studied Si:H films (see Table 1) are shown in Fig. 2.

From various positron annihilation studies on a-Si:H it has been deduced that specific $S/S_{c\text{-}Si}$ values correspond to different types of positron traps, i.e. open volume deficiencies. The following $S/S_{c\text{-}Si}$ values have been reported [3–5]: monovacancies 1.030, divacancies 1.034–1.038, vacancy clusters 1.047–1.061, and microvoids 1.10–1.14. Since the smallest possible stable mass deficiency in silicon at room temperature is the divacancy [7,9], monovacancies are not considered here. Further it is assumed that, depending on the a-Si:H nanostructure, a broad and continuous spectrum of $S/S_{c\text{-}Si}$ values is possible, so the $S/S_{c\text{-}Si}$ ranges of 1.038–1.047 and 1.061–1.10 are not excluded. Using this assumption and the vacancy terminology from Ref. [7], the following three types of dominant positron traps and their corresponding $S/S_{c\text{-}Si}$ values are distinguished: divacancies (<1.038), multivacancies (1.038–1.061), and nanosized voids (>1.061).

Although the matching with the earlier reported $S/S_{c\text{-}Si}$ values is good, it is more important to realise that the trend in $S/S_{c\text{-}Si}$ indicates a considerable variation in nanostructure between the samples. For the amorphous rf-PECVD samples the size of the dominant type of open volume deficiency in the film increases with an increase in deposition rate (due to the increased P_{rf}). This can be understood by realising that at a constant substrate temperature (T_{sub}) a low deposition rate tends to lead to dense films, whereas a high deposition rate results in more porous films [12]. The relatively large increase in $S/S_{c\text{-}Si}$ between samples a3 and a4 may be due to the formation of a short-lived e^+–e^- pair known as positronium (Ps) which can occur if the diameter of the nanosized voids is larger than 0.9 nm. If this is indeed the case, then the voids in film a4 are not likely to be filled with H_2, as this would suppress formation of Ps and hence lower $S/S_{c\text{-}Si}$ [3]. Further analysis

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