IDENTIFICATION OF VACANCY-LIKE DEFECTS IN HIGH-RATE GROWN a-Si BEFORE AND AFTER LIGHT SOAKING BY VEPAS

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ABSTRACT

We show how positron annihilation can distinguish vacancies in undoped hydrogenated amorphous silicon by performing Variable Energy Positron Annihilation Spectroscopy experiments before and after light soaking. We find that vacancy clusters, di-vacancies and a new type of single vacancies are created in undoped as-grown a-Si:H thin film by light illumination. The fact that the vacancy clusters are eliminated by the thermal annealing suggests that the Staebler-Wronski effect is closely related to vacancy clusters in a-Si:H material. The creation of vacancy clusters and redistribution of di-vacancies and even single vacancies probably result in photo-induced structural changes in this material.

INTRODUCTION

Shortly after the realisation of effective doping of hydrogenated amorphous silicon (a-Si:H) [1], it was found that the material suffered from certain light-induced metastable changes (Staebler-Wronski effect (SWE)) [2], which seriously affects its fruitful application.

Although many experiments imply a possible light-induced structural change in a-Si:H, there is no direct evidence of new defects relating to the structural change created by light-soaking, and there are very little experimental data on the microscopic origin of the photo-induced structural change such as photo-induced microvoids. In some of the SWE experiments, only the average effect of the sample is measured so that it can not be directly concluded whether the effect is caused by some changes of inhomogeneous local structure, such as microvoids or clusters, which then spread to the whole sample, or whether the whole network simultaneously responds to the light. As microvoids have been suggested as metastability centres in a-Si:H, especially in high-rate deposited a-Si:H thin film, attention should be focused on microvoid characterisation. Extant annihilation studies on a-Si:H have utilised positron lifetime spectroscopy measurement made with the energetic positrons of the ^{22}Na decay, but the microvoids distribution with depth could not be resolved. In this paper, we use variable energy positron annihilation spectroscopy (VEPAS), by which the depth distribution of microvoids can be revealed, to characterise the microvoids in undoped a-Si:H and show how positron annihilation can distinguish between vacancies in undoped a-Si:H before and after light soaking.

EXPERIMENT

Samples Preparation

The samples in this work were 1μm thick intrinsic a-Si:H thin homogeneous films, grown by pure silane (SiH_4) RF glow discharge PECVD at a deposition rate of 1.5nm/s [3] on quartz substrates. The RF power was 40 Watts, and the substrate temperature was 330°C. The quality of the thin film was evaluated by photo-conductivity measurements. The ratio of photo-conductivity to dark-conductivity of the as-grown film is about 10^5. During the preparation of the film, a mass spectrometer was used to monitor the concentration of SiH_n^+ radicals. To probe the photo-induced defects in a-Si:H, the sample was illuminated by an AM1 light for 350 minutes and Staebler-Wronski effect was observed. The variation of the photo- and dark- conductivity could be annealed away by 1hr thermal annealing at 150°C. However, 40hrs annealing was required to observe annealing of vacancy defects in a-Si:H.

Positron Annihilation Measurement

The positron beam annihilation experiments were performed using a mono-energetic positron beam of intensity $5\times10^4 e^+ s^{-1}$ over an energy range from 0.15 to 25KeV in steps of 250eV, details of which have reported elsewhere [4]. In general, the mean penetration depth x_0 of the positrons implanted at energy E can be determined from the power law $x_0 = AE^n$, where A has been found empirically to be ~400/ρ Å/KeV^n, ρ is the sample density in g/cm^3, x_0 is in Å, E is in KeV, and the power $n \approx 1.6$ for most materials [5]. Thus for a-Si:H (ρ=2.2gcm^{-3}) the maximum positron beam energy 25KeV employed in the present study corresponds to a mean positron stopping depth of about 3μm. This energy range was chosen so that at intermediate positron implantation energies all positrons essentially annihilate in the a-Si:H film while at the highest energies almost full penetration into the quartz substrate could be achieved. Thus, depth profiling may be performed across the entire a-Si:H film.

The 511KeV annihilation γ radiation from the sample was detected with a high purity Ge detector of resolution 1.4KeV at 514KeV and a digitally stabilised multichannel analyser system. A total of 1×10^6 counts were collected under the annihilation photopeak of γ-rays for each positron energy. The photopeak line shape of γ-rays was described using the conventional valence and core annihilation parameters S and W, which are the ratios of counts in the central and wing portions of the annihilation photopeak to the total counts in the peak, respectively. The energy windows were set so that the S parameter represented the fraction of positrons annihilating mainly with valence electrons having a longitudinal momentum component of $p_L \leq 3.7\times10^{-3} m_0c$, where m_0 is the electron mass and c the speed of light. The W parameter, representing the fraction of annihilations with the core electrons, was set to cover the larger momentum component range of $11\times10^{-3} m_0c \leq p_L \leq 29\times10^{-3} m_0c$.

RESULTS AND DISCUSSION

The reduced valence and core electron density at a vacancy increases the lifetime of the trapped positron, and moreover narrows the positron momentum distribution, since the relative proportion of valence to core annihilation increases. Consequently, with increasing number of microvoids, the valence annihilation parameter S increases and the core annihilation parameter W decreases.

Photo-Induced Vacancy-Defects In a-Si:H Thin Film

In principle, an increase in S can be induced by either an increase in the concentration, or a change in the nature, of trapping sites. Information concerning the type of trapping center can be obtained by deducing a defect-specific parameter on the basis of a two-state trapping model. If S_b

and S_v are the characteristic values of the line shape parameter S for positrons annihilating when free and when trapped respectively, a concentration independent characteristic parameter R describing defect type may be defined to be [6],

$$R = \left|(S - S_b)/(W - W_b)\right| = \left|(S_v - S_b)/(W_v - W_b)\right| \tag{1}$$

by assuming only one type of trapping centre is present. Therefore, the number of different vacancy-type positron traps in a-Si:H can be identified by investigating the linearity between the valence and core annihilation parameters. As indicated above, if only a single type of vacancy defect is present, the W parameter depends linearly on the S parameter. The inverse slope of a straight line fit of the W-S plot is the defect characteristic parameter R. This analysis is represented in Figure 1 by plotting the W parameter as a function of the S parameter for VEPAS scans of as-grown, light-soaked, and thermally annealed a-Si:H samples.

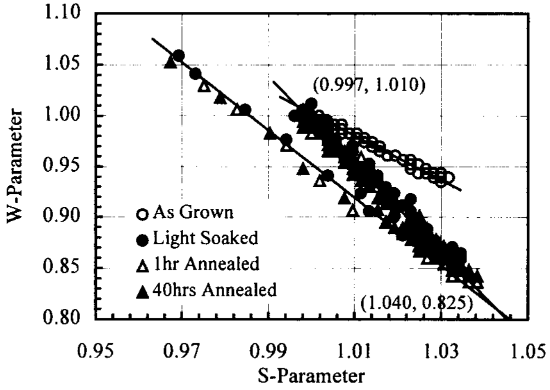

Figure 1. The core annihilation parameter W versus the valence annihilation parameter S, in as-grown, light-soaked, 1hr- and 40hrs annealed a-Si:H materials. The statistical errors of the S and W parameters are $\sigma_S=0.0004$ and $\sigma_W=0.0002$.

It is noted in Fig. 1 that the data for samples after different processing, i.e., as-grown, light-soaked, 1-hr annealed, and 40-hrs annealed a-Si:H thin films, are plotted on the same graph. Despite the variation in depth it can be seen that all the data points for the as-grown a-Si:H thin film fall on the same line in the W-S plane, indicating that vacancy type in the as-grown a-Si:H thin film is the same. The characteristic value of this vacancy is the inverse slope $R = \left|\Delta S/\Delta W\right| \approx 0.48$ of the straight line for the as-grown thin film in Fig. 1. After being light-soaked, it is evident that the (S, W) points are more diversely distributed and form two straight lines, with characteristic R=0.23 for the bulk region and R=0.16 for the surface region, crossing at (1.040, 0.825), implying that two types of vacancies exist in the light-soaked a-Si:H thin film.

The straight line in the (S, W) plane is formed between the end points (S_b, W_b) and (S_v, W_v) corresponding to the delocalised positron state in the bulk and the localised state at the microvoid, respectively. When different types of vacancies exist in the same material, all the straight lines in the (S, W) plane have the same end point at (S_b, W_b). The end points in Fig. 1 are thus an upper limit for the annihilation parameters of the delocalised positron in defect-free a-Si:H thin film, which values are $(S_b, W_b)=(0.997, 1.010)$.

The maximum change of the annihilation parameter S and W compared to the end point (S_b, W_b) gives information on the nature of the microvoid defects detected. In as-grown a-Si:H thin film $S/S_b = 1.035$ and $W/W_b = 0.990$ for both near surface and bulk regions. In a light-soaked sample we obtain $S/S_b = 1.038$ and $W/W_b = 0.998$ for the bulk region but $S/S_b = 1.038$ and $W/W_b = 0.972$ for the near surface region. We suggest that these values for the bulk of the a-Si:H thin film are close to the defect-specific ones, because they are rather independent of processing. Furthermore, they are close to those observed typically for monovacancies in Si [7]. The vacancies formed in the as-grown a-Si:H and in the bulk of light-soaked a-Si:H thin films have thus the open volume of monovacancies, but by contrast, those formed in the near surface region seem to be of a different type.

The relative frequency of core electron annihilations at a vacancy defect depends on the open volume of the defect and on the chemical nature of the surrounding atoms. On the other hand, mainly the valence electrons contribute to the value of the S parameter, which thus depends predominantly on the open volume. Figure 1 shows that for the same value of S the W parameter is clearly higher for the vacancy in the as-grown a-Si:H thin film than for that in the light-soaked a-Si:H thin film. Many more positron annihilations with core electrons are thus recorded at the vacancies in the as-grown than in the light-soaked a-Si:H materials, implying that electrons in the as-grown a-Si:H material give a larger contribution to the W parameter than those in the light-soaked material, which results from the different chemical nature of the vacancies in these two materials.

It is argued that in the absence of defects in a-Si:H material the contribution to the core annihilation rate λ_c of the delocalised positron comes from the *2p* electrons of the Si atoms. If the *2p* shell of the Si atoms gets localised in ***r*** space and overlaps less with the positron wave function due to screening of electrons in the outer shell or that of electron cloud of hydrogen atoms surrounding the Si atoms, a considerably smaller contribution to λ_c will be observed. These arguments suggest that light-soaking creates a new vacancy defect leading more localisation of Si atoms in the a-Si:H thin film, which may be surrounded by T_3^- configurations and T_3^0-T_3^- pairs, implying that light-soaking favours the process $T_4^-+T_4^0 \rightarrow T_3^-+T_3^0$, and thus that metastable defects are created in a-Si:H thin film by light-soaking.

Thermal Annealing Of Vacancy-Like Defects In a-Si:H

Figure 2 precisely shows the depth variation of R parameter obtained for the as-grown, light soaked, 1hr- and 40hrs- annealed a-Si:H thin films. Usually, the R parameter is useful for identifying the trapping site, i.e., the defect type, because it is independent of the of the concentration of the trapping centre. Although the S parameter is sensitive to vacancy-type defects and is generally used to indicate the presence of such defects, it gives ambiguous information on the defect specification because of its dependence on both concentration and type of defect, as was discussed in the forepart of this paper. R parameter of the as-grown a-Si:H material is nearly constant with penetration energy except a little variation in the near surface region, indicating that only a vacancy-type defect exists in the thin film. For the light-soaked a-Si:H thin film, R changes rapidly in the surface region and drops again while the S parameter increases continuously. This suggests that large vacancy clusters were formed during light soaking. Near the surface, where R has a high value, the defects are expected to be di-vacancy and vacancy-clusters of large size, which are formed probably by the agglomeration of three or more vacancies. Thermal annealing lowers the R peak in the R-E plot, showing that the thermal annealing eliminates or probably dissolves the vacancy clusters in the surface region, however, the R value in this region remains high. Presumably this is associated with the dissolving of vacancy clusters and subsequently the aggregation of vacancies with di-vacancies during the thermal annealing process. The drop in R parameters for all the as-grown, light-soaked, 1hr- and 40hrs- annealed a-Si:H thin films in the interior region indicates a transition from large size vacancy cluster to vacancy. It can be seen that the thermal annealing time affects the vacancy type slightly, but the di-vacancies and vacancies in the surface region of a-Si:H thin film in different annealing states have different R parameter level and therefore different characteristics.

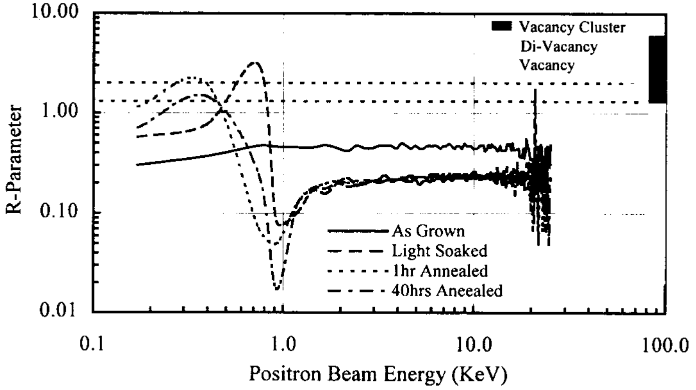

Figure 2. Obtained R parameter for as grown, light-soaked, 1hr- and 40hrs-annealed a-Si:H thin films.

It is worth noting that one hour of thermal annealing changes the peak positions in the R-E plot, both maximum and minimum, compared with that of the light-soaked a-Si:H thin film. This suggests that in the surface region di-vacancies and vacancies resulting from the thermal annealing re-distribute in the surface region during the thermal annealing towards the surface of the samples. However, further annealing time does not further change the distribution. The variation of the position of the di-vacancies and vacancies noted above implies the possibility of movement of photo-induced defects in a-Si:H, which needs to be further probed.

It seems that photo-induced variation occurs mainly in the surface region, as we have already stated. From Fig. 2, the thickness of the surface region is around 550Å, corresponding to 2KeV implantation energy of positrons. For both light-soaked and annealed samples, even though the S parameters change slightly, the R parameters remain constant in the bulk of the samples. Thus only the concentration of trapping centres changes, but the character does not change in this region. However, R takes different values to those for as grown film implying that light-soaking creates different vacancies with different characteristics in the bulk, although they are all of single vacancy type.

Light soaking evidently creates new vacancy-type defects in a-Si:H thin films, with di-vacancies and vacancy clusters in the surface region, and single vacancies in the bulk region. It is shown that thermal annealing removes the vacancy clusters and re-arranges the distribution of both di-vacancies and single vacancies, approaching to a stable state after one hour's annealing, which does not change with further annealing up to 40 hours. We thus suggest that the SWE is closely related to the vacancy cluster defects created in a-Si:H thin films by light illumination. The creation, dissolving of the vacancy clusters, and redistribution of the di-vacancies and the single vacancies during thermal annealing are presumably the microscopic causes of the photodilatation effect [8] in undoped a-Si:H thin films.

CONCLUSIONS

In summary, we have shown how positron annihilation can distinguish between vacancy type defects in undoped hydrogenated amorphous silicon prior to and after light soaking. The vacancy clusters, di-vacancies and a new type of single vacancies are created in undoped as-grown a-Si:H thin film by light illumination. The fact that the vacancy clusters are eliminated by thermal annealing suggests that the SWE is closely related to vacancy clusters in a-Si:H material. The creation of vacancy clusters and redistribution of di-vacancies and even of single vacancies probably result in the photo-induced structural changes in this material.

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