STUDY OF MICROVOIDS IN HIGH-RATE a-Si:H USING POSITRON ANNIHILATION

X. ZOU*, D. P. WEBB*, S. H. LIN*, Y. W. LAM*, Y. C. CHAN*
*Department of Electronic Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
Y. F. HU**, C. D. BELING**, S. FUNG**
**Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

ABSTRACT

In this paper, we have carried out the positron annihilation measurement on high-rate and low-rate a-Si:H thin films deposited by PECVD. By means of the slow positron beam Doppler-broadening technique, the depth profiles of microvoids in a-Si:H have been determined. We have also studied the vacancy-type defect in the surface region in high-rate grown a-Si:H, making comparison between high-rate and low-rate a-Si:H. By plotting S and W parameters in the (S, W) plane, we have shown that the vacancies in all of the high-rate and low-rate deposited intrinsic samples, and in differently doped low-rate samples are of the same nature.

INTRODUCTION

Amorphous tetrahedral semiconductors are potential candidates for the fabrication of micro- and opto-electronic devices. Advances in this area have, however, been hindered by the limited understanding of their structure, and thus electronic properties, even at the most elementary level. For instance, light-induced degradation of hydrogenated amorphous silicon alloy materials and devices has been the subject of intensive studies, but the origin of the metastability has not been unambiguously identified. Microvoids have also been suggested as metastability centers in a-Si:H, especially in high-rate deposited a-Si:H thin film. Therefore, attention should be focused on microvoids characterization.

Using the small-angle X-ray scattering (SAXS) measurement, it has been demonstrated[1,2] that even in the best quality material, microvoids of typical diameter 1.0nm exist, occupying a volume fraction of about 1%. The void density is typically larger for poorer quality material[3]. A correlation between the microvoid density in the material with the initial and light-degraded performance of solar cells in which the intrinsic layer has varying microvoid densities caused by changes in the deposition rate has also been established[4]. The depth profile and type of microvoids in a-Si have, however, been less reported. In this paper, we will use positron beam annihilation to characterise the microvoids in a-Si:H high-rate deposited with deposition rate over 1.5nm/s, in an attempt to clarify the details of microvoids in a-Si:H.

EXPERIMENTAL DETAILS

Samples Descriptions

The samples in this work were 1μm intrinsic a-Si:H thin homogenous films grown by pure silane (SiH_4) RF glow discharge PECVD at the deposition rate of 1.5nm/s on quartz substrates, and 1μm p- and n-type a-Si:H film deposited by glow discharge using gas mixture of (SiH_4+B_2H_6+H_2) and (SiH_4+PH_3+H_2) at a deposition rate of 0.2nm/s on quartz substrates. For

Mat. Res. Soc. Symp. Proc. Vol. 467 © 1997 Materials Research Society

both the dopants the gas ratio was about 7×10^{-3}. For comparison, the deposition conditions were varied with RF power between 8 and 40 Watts, and with substrate temperature between 280°C and 330°C. The quality of the thin films was evaluated by photo conductivity measurements, which indicated that the ratio of photo conductivity and dark conductivity of the intrinsic films is about 5 orders, and the magnitude of conductivity of p- and n-type a-Si:H are $10^{-2}\Omega^{-1}cm^{-1}$ and $10^{-1}\Omega^{-1}cm^{-1}$, respectively.

Positron Beam Annihilation Measurement

The positron beam annihilation experiments were performed using a positron beam over on the energy from 0 to 25keV. The penetration depth of the positron beam at energy E can be determined from the following power law[5]

$$\bar{z} = AE^{n} \tag{1}$$

which was originally developed for electron stopping. The constant A in equation (1) was found empirically to be $A \sim 400/\rho$ $\text{Å}/keV^{n}$, where ρ is the a-Si:H density in g/cm^{3}, $\bar{z}$ is in Å, E is in keV, and the power $n\approx1.6$ for positrons incident on most materials. Thus the maximum positron beam energy $25keV$ corresponds to a mean positron stopping depth of about 3μm. This energy range was chosen so that at a certain positron penetration energy all positrons annihilate in the a-Si:H film and depth profiling of positron annihilation could be performed across the entire a-Si:H film.

The Doppler broadened shape of the $511keV$ annihilation radiation was measured with a Ge detector and described with the conventional valence and core annihilation parameters S and W. The S parameter represents the fraction of positrons annihilating mainly with the valence electrons with a longitudinal momentum component of $p_L\leq3.7\times10^{-3}m_0c$, where m_0 is the electron mass and c the speed of light. The W parameter is the fraction of annihilation with the core electrons with a large momentum component of $11\times10^{-3}m_0c\leq p_L\leq29\times10^{-3}m_0c$.

RESULTS AND DISCUSSIONS

Positrons get trapped at neutral and negative vacancy defects because of the missing positive charge of the ion cores. Consequently, with increasing number of microvoids, the valence annihilation parameter S increases and the core annihilation parameter W decreases. A trapped positron at a vacancy overlaps mainly with the core electrons of the nearest neighbour atoms. Hence the shape and magnitude of the core electron momentum distribution can be used to identify the nature of the vacancy acting as a positron trap.

Microvoids At Surface Region In High Rate Deposited a-Si:H

Figure 1 shows the positron line-shape parameter S measured vs. incident energy for a-Si:H thin films prepared at different process conditions. A general trend is observed in all samples. The depth dependencies of the microvoids are clearly visible in these results, as well as the deposition condition dependencies. The measured S parameters are about 0.565 to 0.579 at low positron implanting energy. This is attributed to positrons annihilating within the surface region.

As the implanting energy increases, more positrons annihilate in the bulk of a-Si:H and this results in an increase of the S-parameter to a value of about 0.583, which could be seen as the characteristic value of a-Si:H. The S-parameter decreases with further increase in positron implanting energy as more positrons annihilate in the bulk of the quartz substrate and finally approaches the same value for all samples.

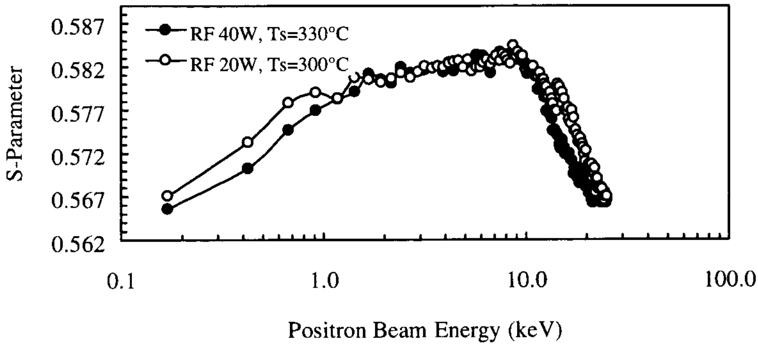

Figure 1. A Doppler-broadening line-shape parameter S as a function of incident positron energy for high-rate deposited a-Si:H thin film with different RF power and substrate temperature by PECVD. The filled circle curve is the results of a-Si:H under RF power of 40W, and substrate temperature of 330°C, and the open circles for RF power of 20W, and substrate temperature of 300°C.

It can be easily seen that for high rate deposited a-Si:H thin films with different RF power and substrate temperature, the microvoid profile appears the same in the bulk, but obvious differences exist in the surface region for positron beam incident energy below 1keV, corresponding to about 180Å according to equation (1). It seems that higher RF power and substrate temperature is of benefit in eliminating microvoids within the surface region of high-rate deposited a-Si:H. This is mainly due to the different status of monosilicon radicals when the RF glow discharge is off. The relevent reactions are:

$$e^- + SiH_4 \rightarrow SiH_2 + H_2 + e^- \qquad 2.2eV \qquad (2\text{-}1)$$
$$e^- + SiH_4 \rightarrow SiH_3 + H + e^- \qquad 4.0eV \qquad (2\text{-}2)$$
$$e^- + SiH_4 \rightarrow Si + 2H_2 + e^- \qquad 4.2eV \qquad (2\text{-}3)$$
$$e^- + SiH_4 \rightarrow SiH + H_2 + H + e^- \qquad 5.7eV \qquad (2\text{-}4)$$

The corresponding electron threshold energies are as labelled. As is well known, the number of vacancies is tightly related to that of SiH_2[6]. Comparing with a-Si:H deposited with RF power of 20W and substrate temperature of 300°C, if RF power is higher, say 40W, and the substrate temperature is 330°C, the reaction process described by (2-2), (2-3), and (2-4) will dominate the glow discharge and amounts of radical SiH_2, as well as the residual radical SiH_2, will decrease, which is conducive to eliminating microvoids within the surface region of high-rate grown a-Si:H by PECVD.

<u>Deposition Rate Effects On Microvoids: Comparison With Low Rate Deposited a-Si:H</u>

Low rate grown a-Si:H thin films exhibit fewer microvoids both within the surface region and in the bulk compared to high-rate grown films, which can be seen from the comparison plotted in

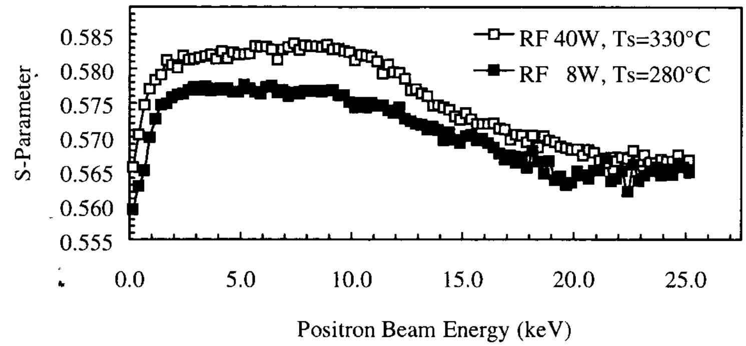

Figure 2. Comparison of S parameters between high- and low-rate grown a-Si:H. The filled circle curve is for low-rate a-Si:H with deposition rate of 0.2nm/s, and the open circle for high-rate a-Si:H with deposition rate of 1.5nm/s.

figure 2. Again a clear correlation between microvoids and deposition process conditions is apparent. As the deposition rate of the low rate process is about 0.2nm/s, which was carried out by hydrogen-diluted silane glow discharge with RF power of 8W, the dominant process should be that described by (2-2) because of the hydrogen depression of reaction (2-1). Therefore, the

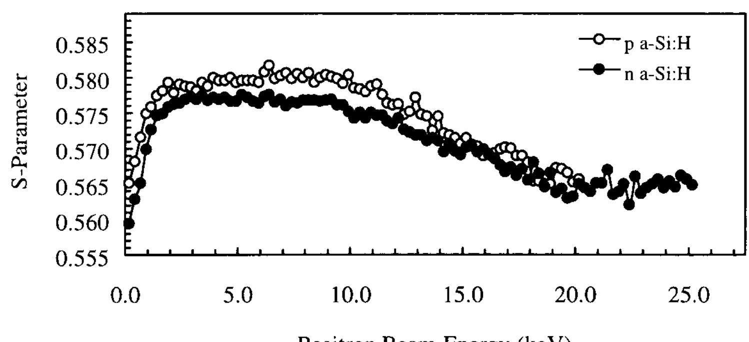

Figure 3. Dopants effects on S-parameters of a-Si:H. Both p- and n-type a-Si:H have been prepared under RF power of 8W, and substrate temperature of 280°C.

monosilicon radical SiH_3 is in the majority in low-rate PECVD process, and consequently fewer microvoids exist in low-rate grown a-Si:H than that in high-rate deposited a-Si:H.

Effects Of Doping Species On Microvoids

Study of dopant effects on microvoids were also carried out in this work, and S-parameters of p- and n-type a-Si:H are illustrated in figure 3. It indicates that the boron dopant induce more microvoids than the phosphorous dopant. It is worth studying the native vacancies that could affect the doping efficiency in a-Si:H, i.e., n-type doping is easier than p-doping. Is there any common microscopic nature between p- and n-type a-Si:H?.

Identification Of Vacancy Nature In Both High-Rate And Low-Rate Grown a-Si:H

The number of different vacancy-type positron traps in a-Si:H can be studied by investigating the linearity between the valence and core annihilation parameters[7]. If only a single type of vacancy defect is present, the W parameter depends linearly on the S parameter. The inverse slope of the S-W plot is the defect characteristic parameter represented by $R=(S_v-S_b)/(W_b-W_v)$, where "*b*" stands for end point and "*v*" for vacancy.

In figure 4 the data in all of the samples lie on a straight line in the (S, W) plane, which

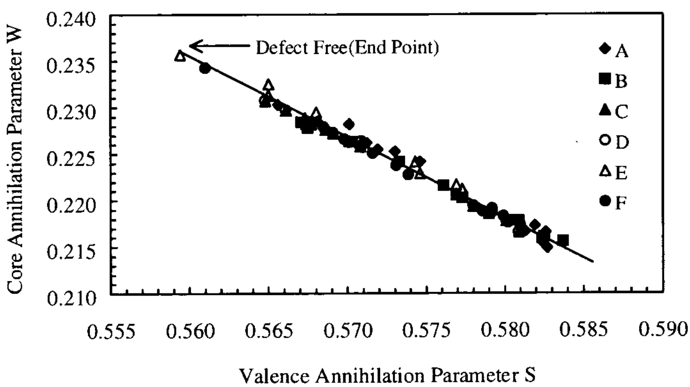

Figure 4. The core annihilation parameter W vs the valence annihilation parameter S, in all of the high- and low-rate grown a-Si:H thin films. The annihilation parameters in defect-free thin films are indicated. The statistical errors of the S and W parameters are $\sigma_S=0.0004$ and $\sigma_W=0.0004$. (A)HRI01: RF=40W, T_s=330°C. (B)HRI02: RF=20W, T_s=300°C. (C)LRP01: RF=20W, T_s=280°C. (D)LRP02: RF=8W, T_s=280°C. (E)LRN01: RF=20W, T_s=280°C. (F)LRN02: RF=8W, T_s=280°C.)

indicates that a single type of vacancy explains all the positron annihilation results in intrinsic high-rate and low-rate deposited, and p- and n-type doped low-rate deposited a-Si:H homogeneous thin films. This vacancy can be characterized by the slope $R=|\Delta S/\Delta W|\approx1.2$ of the solid line in figure 4.

The straight line in the (S, W) plane is formed between the end points (S_b, W_b) and (S_{vi}, W_{vi}) corresponding to the delocalized positron state in the bulk and the localized state at the vacancy *i*, 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 point in figure 4 determines thus the annihilation parameters of the delocalized positron in defect free a-Si:H thin film, which lies at $(S_b, W_b) = (0.559, 0.236)$.

The maximum change of the annihilation parameters S and W compared to the end point (S_b, W_b) gives further information on the nature of detected vacancy defects. Summarized in table 1 are maximum S/S_b and W/W_b ratios of all samples individually.

Table 1 Summary of maximum change of annihilation parameters S and W

Sample Code	HRI01	HRI02	LRP01	LRP02	LRN01	LRN02
Max. S/S_b	1.044	1.045	1.041	1.041	1.033	1.040
Max. W/W_b	0.976	0.971	0.980	0.980	0.998	0.993

We may conclude that these values are close to the defect characteristic ones (S_{vi}, W_{vi}), because they are rather independent of the doping type and deposition process.

CONCLUSIONS

In summary, we have carried out the positron annihilation measurement on high-rate and low-rate a-Si:H thin films deposited by PECVD. By means of the slow positron beam Doppler-broadening technique, the depth profiles of microvoids in a-Si:H have been resolved. We have also studied the vacancy-type defect in the surface region in high-rate grown a-Si:H, and made comparison between high-rate and low-rate a-Si:H. By plotting S and W parameters in the (S, W) plane, we have identified that the vacancies in all of the high-rate and low-rate deposited intrinsic a-Si:H, and low rate differently doped a-Si:H films are of the same nature. We would like to point out that although we see a correlation between deposition conditions and voids depth profiles in all different samples, these results should be considered only to depict the trend under certain deposition parameters. To conclude, positron annihilation is a powerful technique to characterize vacancy-type defects in a-Si:H, especially to give a depth profile of such defects, which is useful for the characterization of multilayered thin film structures.

REFERENCES

1. D. L. Williamson, A. H. Mahan, B. P. Nelson and R. S. Crandall, J. Non-Crst. Solids **114**, p. 226 (1989).

2. A. H. Mahan, D. L. Williamson, B. P. Nelson and R. S. Crandall, Phys. Rev. B **40**, p. 12,024 (1989).

3. A. H. Mahan, D. L. Williamson, B. P. Nelson and R. S. Crandall, Solar Cells **27**, p.465 (1989).

4. S. Guha and J. Yang, Appl. Phys. Lett. **61**, p. 1,444 (1992).

5. Peter J. Schultz and K. G. Lynn, Reviews of Modern Physics **60**, p. 701 (1988).

6. Werner Luft and Y. Simon Tsuo, Hydrogenated Amorphous Silicon Alloy Deposition Processes, Marcel Dekker, Inc., New York • Basel • Hong Kong, 1993, pp. 15-17.

7. L. Liszkay, C. Corbel, L. Baroux, P. Hautojärvi, M. Bayhan, A. W. Brinkman and S. Tatarenko, Appl. Phys. Lett. **64**, p. 1,380 (1994).