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ScienceDirect
Radiation Physics and Chemistry 76 (2007) 220–223
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Positron annihilation and constant photocurrent method measurements on a-Si:H films: A comparative approach to defect identification

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Abstract

Defect structure of hydrogenated amorphous silicon thin-films was studied by positron annihilation spectroscopy (PAS), whereas the density of states below the Fermi level was measured by constant photocurrent method (CPM). Divacancies and large vacancy clusters were identified as the main defects present in these films, with relative concentrations strongly dependent on the rf-power. Correlation between PAS, CPM results and $I(V)$ characteristics of solar cells suggests the creation of energy levels above the Fermi energy, not observable by CPM, related to large vacancy clusters.

Keywords: Variable-energy positron annihilation; Doppler broadening; Constant photocurrent method; Defects; a-Si:H; Density of states

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is a thin-film semiconductor with increasing importance from both technological and scientific points of view. It has a wide variety of applications in microelectronics and optoelectronics, particularly in thin film transistors for photovoltaics and display applications. The most commonly used deposition technique for industrial production of a-Si:H films is plasma enhanced chemical vapor deposition (PECVD) (Abelson, 1993).

The electrical and optical properties of the a-Si:H films are controlled by the localized states in the band gap, the dangling bond being the principal defect state inside the band gap of a-Si:H. Dangling bonds are most likely associated with small multivacancy complexes (divacancies, trivacancies, etc.) within the disordered tetrahedrally coordinated network.

In this work, the density of a-Si:H electronic deep defects was studied by CPM measurements; the techniques of positron annihilation spectroscopy (PAS) were used to investigate the defect structure, particularly vacancy type defects. In order to better understand the correlation between both results, the performance of solar cells based on a-Si:H thin-films was also studied by $I(V)$ measurements.

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0969-806X/$ - see front matter
doi:10.1016/j.radphyschem.2006.03.040

PAS features techniques suited for the study of the electron density and electron momentum density around the defects. These methods might be employed in the study of semiconductors (Krause-Rehberg and Leipner, 1999a) as bulk techniques or in low-energy positron experiments for near-surface and thin-film studies like in our case, performing Doppler broadening experiments using a slow positron beam (Lima et al., 1999). In defect studies, the annihilation lineshape is often characterized in terms of two parameters, S and W e.g. (Krause-Rehberg and Leipner, 1999b), corresponding to the fractions of annihilation with low-momentum (valence) and high-momentum (core) electrons, respectively. The low-momentum fraction, S, depends primarily on size and concentration of open volume defects, whereas the high-momentum fraction, W, is sensitive to the electronic structure at the annihilation site. Together, these two parameters form a unique signature for different defect structures (Liszkay et al., 1994).

The constant photocurrent method (CPM) (Vanecek et al., 1981), was used to measure the subgap absorption coefficient of the amorphous semiconductor samples. In CPM, the impinging monochromatic photon flux is adjusted, at each wavelength, so as to maintain a constant photocurrent. In the assumption of a constant conduction electron generation rate the inverse of the photon flux is proportional to the absorption coefficient, α_{CPM}. The density of deep states (DOS) can be determined from the sub-band-gap absorption spectra in a-Si:H using the ‘‘single energy’’ technique (Wyrsch et al., 1991).

2. Experimental

The a-Si:H films were deposited by magnetically confined rf (13.56 MHz) PECVD on crystalline silicon (c-Si) for PAS studies, and on alkali-free glass substrates for CPM measurements, according to the following optimised deposition conditions: substrate temperature, $T_S = 250\,°C$; deposition pressure, 200 mTorr; SiH_4 flow, $F_{SiH_4} = 20$ sccm and magnetic field, $B = 160$ G. The rf power, P, varied between 5 and 40 W. The thickness of the films was about 600 nm for all the samples. The positron beam Doppler broadening measurements were performed varying the positron energies from 0.1 to 30 keV (Lima et al., 1999) on the a-Si:H films deposited on c-Si. The DOS values were determined from CPM spectra (Wyrsch et al., 1991) using a Kracos monochromator with light intensity adjustment. The density of deep defects was calculated from $N_{dd} = C_{ref} \times \alpha(E_{ref})$, with $C_{ref} = 10^{16}\,cm^{-2}$ and $E_{ref} = 1.2$ eV.

Solar cells based on intrinsic a-Si:H with the structure (ITO/p–i–n/Al) were also prepared. Indium tin oxide (ITO) films were deposited by reactive thermal evaporation (RTE). Aluminium films were deposited by thermal evaporation. Undoped a-Si:H films were deposited using rf powers of 10, 20 and 30 W under the previously referred conditions. Doped n and p layers were deposited also by PECVD using PH_3 or B_2H_6 and CH_4 as dopants, respectively.

3. Results and discussion

The Doppler parameters, S_{film} and W_{film}, and the positron diffusion length, L_+, of each a-Si:H film deposited on c-Si were obtained fitting the S(E) and W(E) data using VEPFIT (van Veen et al., 1990) assuming samples consisting of two layers, one being the a-Si:H film and the c-Si substrate the other.

Fig. 1a shows the S_{film} parameter normalized to $S_{c\text{-}Si}$ for various a-Si:H films deposited at different rf powers. The normalized S_{film} parameter reaches a maximum already at a relatively low rf power value and decreases then steadily. On the other hand, the linear behaviour of the S_{film}–W_{film} plot (Fig. 1b) strongly suggests that in these films two types of open volume defects are present, leading to competing trapping at a near-saturation level. The relative concentration of those trapping sites is dependent of the rf power deposition. The experimental boundary values of the S_{film} are ~1.027 and ~1.06. In

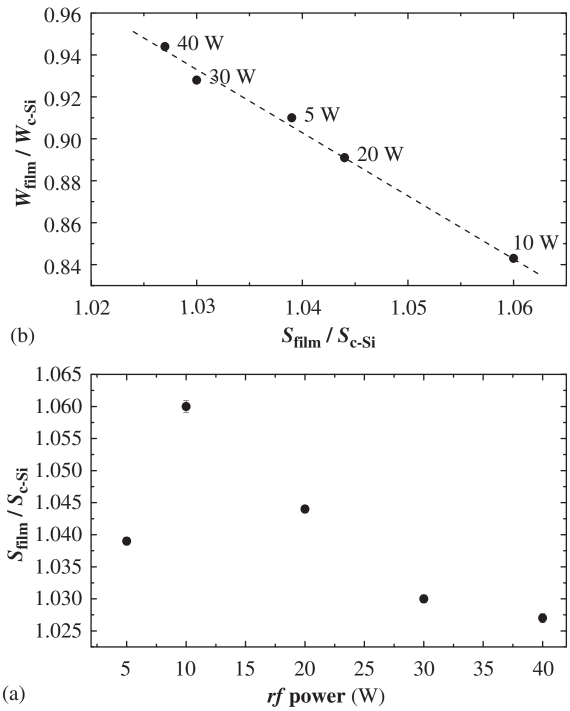

Fig. 1. (a) Normalized S_{film} and (b) S–W plot, for films deposited at different rf powers.

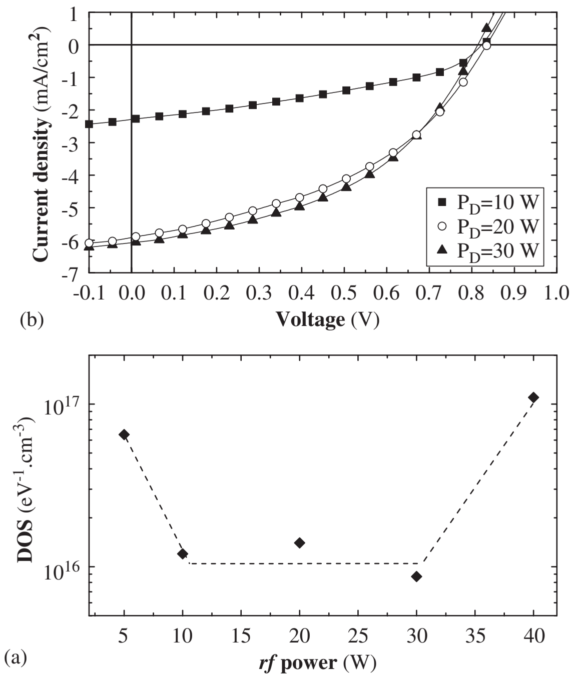

Fig. 2. (a) Deep states density as a function of the rf deposition power. (b) Current density vs. applied voltage for the solar cells prepared with a-Si:H films.

principle, four defect types which may trap positrons can be considered in a-Si:H (Zou et al., 2000; Amarendra, 2002): monovacancy, divacancy, small vacancy cluster (with ~5 Si atoms missing) and large vacancy clusters or microvoids with a diameter of 1–2 nm, where positronium (Ps) can also be formed. Indeed, our maximum and minimum S_{film} values might correspond to trapping in large vacancy clusters/microvoids and in small vacancy type defects (probably divacancies), respectively. The highest S_{film} value may also include contributions from positron surface states and from Ps caged inside cavities.

Fig. 2a presents the variation with the rf power of DOS (below E_{F}) as obtained from CPM measurements. For the lowest and the highest rf powers the DOS values are about one order of magnitude higher than in the range of 10–30 W, where the films reach the typical value for good quality films ($10^{16}\,\mathrm{eV^{-1}\,cm^{-3}}$). The highest DOS values observed at 5 and 40 W may be interpreted by an incomplete passivation of the dangling bonds either due to insufficient hydrogen incorporation (as expected at the lowest rf power) or due to the strong damage caused by the ion bombardment leading to the bond-breaking or to the release of hydrogen previously incorporated (as expected to occur at high rf power). The films produced at powers between 10 and 30 W exhibit quite different defect structures as observed by PAS, whereas the DOS values indicate similar deep state densities below the E_{F}. The film deposited at 10 W reveals large vacancy clusters as the main positron traps while at 30 W divacancies are dominant.

The influence of these defect types on the optoelectronic properties of a-Si:H films was also studied. The current density as a function of the applied voltage under AM1 illumination conditions was measured on solar cells prepared with a-Si:H films grown at rf powers of 10, 20 and 30 W maintaining the other deposition conditions constant. In Fig. 2b the *V–I* curves obtained for these solar cells are presented. The poorest cell performance is observed on the solar cell prepared with 10 W, and the best performance is achieved for the film fabricated with 30 W. The high concentration of large vacancy-type defects in the 10 W film results in a lower current density. Two reasons can contribute to this behaviour: the film with higher concentration of large vacancy clusters has a lower mass density and consequently the incident light produces less electron–hole pairs per unit volume and an increase of the DOS above the Fermi level. This fact has indeed been reported before (Babras et al., 1990) in a-Si:H films studied by deep level transient spectroscopy, photoluminescence and spectroscopic ellipsometry. These levels, related to large vacancy clusters, may also act as charge recombination centres and are not attainable by CPM, which determines the DOS below the Fermi level. Moreover, the incident 1.2 eV photons not only promote electron transitions from deep states inside the bandgap to the conduction band (being the dominant contribution to the measured photocurrent), but can also promote electronic transitions from the valence band up to those levels related to large vacancy clusters, which do not contribute to the photocurrent measured by CPM (Schmidt and Rubinelli, 1998; Schmidt et al., 2000). Consequently, for higher concentrations of large vacancy clusters a higher light intensity is needed to keep the generated photocurrent constant but leading then to an underestimation of the DOS value when determined by this method.

4. Conclusions

PAS was used to characterize the defect structure of a-Si:H films deposited by PECVD on c-Si substrates. Two dominant defect types were identified, large vacancy clusters and divacancies. The DOS below E_{F} was measured by CPM using the "single energy technique". From the comparison of PAS and CPM results with the performance of solar cells, the existence of states above the Fermi energy and inside the bandgap, related to the presence of large vacancy clusters in a-Si:H films, was evidenced. These levels influence the recombination of charge carriers, cause an underestimation of DOS values determined by "single energy" CPM measurements, and contribute to the weaker performance of a-Si:H solar cells with high concentration of large vacancy clusters.

Acknowledgements

The support provided by the Hungarian-Portuguese Bilateral Scientific agreement TET No. P23/03 is gratefully acknowledged.

References

Abelson, J.R., 1993. Plasma deposition of hydrogenated amorphous silicon: studies of the growth surface. Appl. Phys. A 56, 493–512.

Amarendra, G., 2002. Positron annihilation studies of vacancy defects in crystalline and amorphous Si. Defects and Diffusion in Semiconductors IV 200–202, 189–217.

Babras, S., Rajarshi, S.V., Dusane, R.O., Bhide, V.G., Kshirsagar, S.T., 1990. Effect of rf power on the structure and related gap states in hydrogenated amorphous silicon. J. Non-Cryst. Solids 119, 342–346.

Krause-Rehberg, R., Leipner, H.S., 1999a. Positron Annihilation in Semiconductors–Defect Studies. Springer, Berlin, Heidelberg, pp. 1–4.

Krause-Rehberg, R., Leipner, H.S., 1999b. Positron Annihilation in Semiconductors–Defect Studies. Springer, Berlin, Heidelberg, pp. 21–24.

Lima, A.P. de, Lopes Gil, C., Gordo, P.M., Duarte Naia, M., 1999. Initial results with a variable energy positron system at Coimbra. In: OECD/NEA (Ed.), Workshop on Ion and Slow Positron Beam Utilization, Costa da Caparica, Portugal, pp. 121–128.

Liszkay, L., Cordel, C., Baroux, L., Hautojärvi, P., Bayhan, M., Brinkmann, A.W., Tatarenko, S., 1994. Positron trapping at divacancies in thin polycrystalline CdTe films deposited on glass. Appl. Phys. Lett. 64, 1380–1382.

Schmidt, J.A., Rubinelli, F.A., 1998. Limitations of the constant photocurrent method: a comprehensive experimental and modelling study. J. Appl. Phys. 83, 339–348.

Schmidt, J.A., Koropecki, R.R., Arce, R.D., Rubinelli, F.A., Buitrago, R.H., 2000. Energy-resolved photon flux dependence of the steady state photoconductivity in hydrogenated amorphous silicon: implications for the constant photocurrent method. Thin Solid Films 376, 267–274.

Vanecek, M., Kocka, J., Stuchlík, J., Triska, A., 1981. Direct measurement of the gap states and tail absorption by constant photocurrent method in amorphous silicon. Solid State Commun. 39, 1199–1202.

van Veen, A., Schut, H., Haakvoort, J., Vries, R.A., Ijpma, M.R., 1990. Analysis of positron Profiling Data by Means of "VEPFIT". In: Schultz, P.J., Massoumi, G.R., Simpson, P.J. (Eds.), Positron Beams for Solids and Surfaces. AIP Conference Proceedings, vol. 218. London, Ontario, Canada, pp. 171–196.

Wyrsch, N., Finger, F., McMahon, T.J., Vanecek, V., 1991. How to reach more precise interpretation of subgap absorption spectra in terms of deep defect density in a-Si:H. J. Non-Cryst. Solids 137–138, 347–350.

Zou, X., Chan, Y.C., Webb, D.P., Lam, Y.W., Hu, Y.F., Beling, C.B., Fung, S., Weng, H.M., 2000. Photoinduced dehydrogenation of defects in undoped a-Si:H using positron annihilation spectroscopy. Phys. Rev. Lett. 84, 769–772.