

Aging effects in microcrystalline silicon films studied by transient photoconductivity

V. Smirnov ^a, S. Reynolds ^a, C. Main ^a, F. Finger ^b, R. Carius ^b

^a School of Computing and Advanced Technologies, University of Abertay Dundee, Bell Street, Dundee DD1 1HG, UK
^b IPV, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

Measurements of dark conductivity, steady-state and transient photoconductivity in undoped and boron-doped microcrystalline silicon films exposed to room air are reported. Two aging processes are identified: (i) an increase in dark conductivity and mobility-lifetime product occurring over several days, that may be reversed by heating to 160 °C under vacuum, and subsequently re-cycled, (ii) an irreversible change in the density of states occurring over a period of several months. It is proposed that the reversible effect is associated with charge transport in a region of electron accumulation induced by weakly-adsorbed water, whereas the irreversible effect, identified from its transient photocurrent signature, is associated with a true change in the density of states within the transport path, possibly as a result of slow chemical reactions at silicon grain boundaries.

PACS: 73.50.Gr; 73.61.Tm; 73.50.Pz; 73.20.Hb

1. Introduction

Both reversible and irreversible changes in conductivity have been reported to occur in amorphous silicon (a-Si:H) [1] and microcrystalline silicon (μ -Si:H) [2] films exposed to atmospheric gases. These are brought about by surface chemical reactions such as oxidation, which are not readily reversible, and by weaker processes involving physical adsorption through Van de Waals forces or coordination of orbitals, which may be reversed, for example, by vacuum drying. The interaction between dangling bonds, hydrogen and adsorbed species introduces further complications. Consequent changes will occur in the density and charge of surface and interface states, which may in turn influence bulk conductivity through modification of surface space charge layers [3]. Of the components of room air, it has been suggested that water vapor may be responsible for conductivity increases [1], and oxygen for conductivity decreases [2]. There is continuing interest in the effects of atmospheric aging in μ -Si:H films prepared for photovoltaic applications [4, 5 and 6]. Correlations of changes in conductivity, spin density and infrared absorption on aging with film structure and morphology have recently been reported [4].

Here, we present a preliminary study of steady-state and transient coplanar photoconductivity (SSPC and TPC, respectively) in device-quality μ -Si:H films exposed to room air for varying periods ('aging') following by heating to 160 °C under vacuum ('annealing'). TPC can provide energy-resolved

information on the electronic density of states (DOS), and has recently been shown to be a sensitive tool in the study of light-induced metastable defect creation [7]. It may therefore prove useful in identifying any changes in the DOS that may occur during aging. Our purpose here is not to resolve these complex and intriguing phenomena, but primarily to determine whether such measurements might be of use in a future, more comprehensive, programme.

2. Experimental

μ -Si:H films were deposited at IPV Jülich by PECVD [8] at 95 MHz, at a gas pressure of 300 mTorr, a silane concentration $SC=[SiH_4]/([SiH_4] + [H_2])$ between 3% and 7% and an RF power of 8 W, onto borosilicate glass substrates maintained at 200 °C. Metal contacts 5 mm in length separated by a 0.5 mm gap were deposited to form a gap cell. The annealing procedure consisted of heating the sample in a vacuum of 10^{-3} Torr to 160 °C for typically 10 minutes. Prolonged heating at this temperature was found to have no further measurable effect on the sample. Aging was performed simply by storing the sample in air in the laboratory.

All electrical measurements were carried out at a bias of 300 V. Steady-state currents were measured using a Keithley 617 electrometer, and a calibrated red LED (620 nm) was used as the light source in SSPC work. Our transient photocurrent measurement system and data analysis procedures have been described

elsewhere [9]. A red laser (640 nm) plus neutral density filters was used to generate a pulsed photocarrier density of approximately 10^{16} cm^{-3} .

3. Results and discussion

3.1. Dark conductivity

The trend in dark conductivity normally observed on aging and annealing [4] is illustrated in Fig. 1(a). At low SC, where crystalline, more porous films are expected, dark conductivity decreases on aging in room air for 10 days and may be reversed on annealing. At higher SC, close to the transition from microcrystalline to amorphous growth, films behave in the opposite sense.

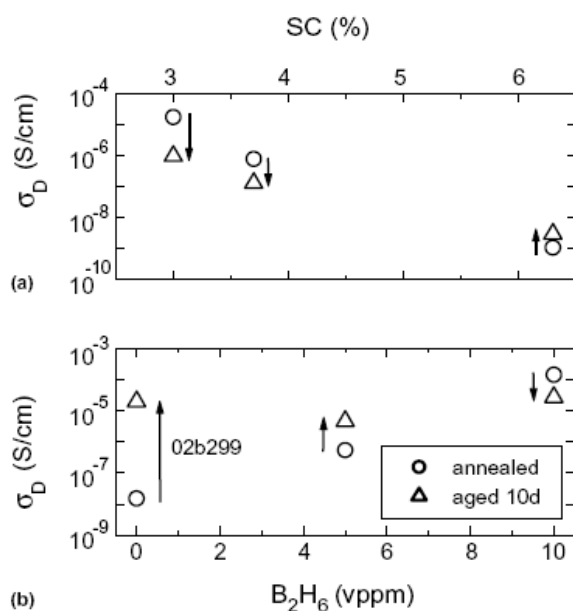


Fig. 1. Variation in dark conductivity σ_D for aging-annealing cycles: (a) vs. silane concentration, (b) vs. boron doping.

We have also studied a series of boron-doped samples, shown in Fig. 1(b). The nominally undoped film (sample 02b299) shows a reversible increase in dark conductivity of some three orders of magnitude after 10 days' aging. At a diborane concentration of 5 vppm, the conductivity increase after aging is reduced by two orders of magnitude to a factor of 10, and at 10 vppm there is a factor of 10 decrease in conductivity. This suggests boron doping shifts the Fermi level so as to oppose the effects of aging, e.g. to reduce the build-up of an electron accumulation layer. At 5 vppm, aging dominates and the conduction path becomes n-type, but at 10 vppm boron doping dominates and the conduction path remains p-type, albeit with a reduced carrier density. If this reasoning is correct, then careful observation of the 5 vppm sample conductivity should

reveal a dip as aging proceeds, as the Fermi level effectively traverses the band-gap. This is currently under investigation.

Although the boron-doped series was found from Raman scattering measurements to be highly crystalline, note that a strong increase in conductivity was exhibited by the nominally undoped sample on aging. Such behaviour is more commonly, although not exclusively, associated with more compact films grown at higher SC [4], and may be due to residual boron doping as evidenced by the low dark conductivity after annealing.

3.2. Steady-state photoconductivity

Changes in $\mu\tau$ -product vs. dark conductivity for sample 02b299 over the 10 days following annealing are shown in Fig. 2. The conductivity increases by some three orders of magnitude (an effective shift in the Fermi level relative to

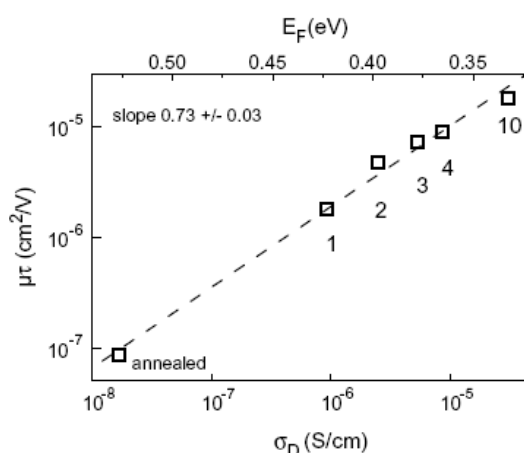


Fig. 2. Mobility-lifetime product vs. dark conductivity for sample 02b299, aged over a period of 10 days.

the transport level of 0.2 eV), whereas the $\mu\tau$ -product increases by some two orders. The relationship fits a power law, of index approximately 0.7. A similar trend, though with considerably greater scatter, has been observed in both a-Si:H and μ c-Si:H [10, 11] where the Fermi level position has been shifted either by intentional doping, or by inadvertent doping by impurities incorporated during deposition. The majority carrier lifetime is increased by the filling of deep defects which thus may no longer act as recombination centers. Here, separation of carriers by surface band-bending [12] could also contribute. Changes in the photoconductivity index, γ , from 0.7 in the annealed state to 0.5 after 10 days aging also occur, as shown in Fig. 3, consistent with a movement of the Fermi level towards the band edge [13].

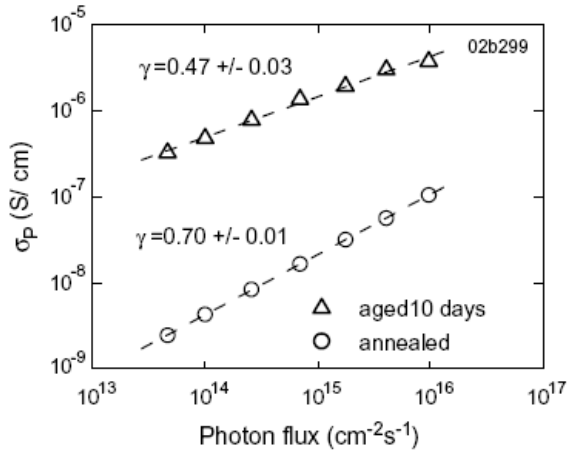


Fig. 3. Photoconductivity σ_P vs. photon flux for sample 02b299, in annealed state and after aging for 10 days.

3.3. Transient photoconductivity

Two sets of TPC decays, taken on the same sample 02b299, are shown in Fig. 4. One set shows the behaviour some two weeks after deposition ('as-received'), and the other was taken after 6 months exposure to room air. In all cases, the sample was annealed, returned to room temperature, the photocurrent decay recorded without breaking vacuum, and then aged in room air over 10 days. Several TPC decays were taken over this period to track any changes. The general trend observed is similar for both sets of measurements – there is an initial fall in current, steeper than t^{-1} , which reduces in gradient after approximately 1 μ s. The effect of aging is primarily to reduce the extent of the initial fall, although changes in slope also occur. This feature is associated with deep trapping, and thus the deep defect density is apparently higher in the as-received samples. Fig. 5 shows the DOS distributions extracted using a Fourier-transform technique [9]. From TPC measurements at 200 K (not shown here) we were able to determine an aging-independent conduction band tail slope of approximately 23 meV.

Fig. 5(a) reveals a pronounced peak in the DOS for the as-received sample, of order 10^{17} cm^{-3} centered at about 0.5 eV. As short-term aging proceeds, the peak moves to shallower energies. However, it is unclear whether this reflects a true change in the DOS, or a change in occupancy within the same DOS caused by an effective shift in the Fermi level. A dark-current activation energy of 0.55 eV in the annealed state indicates that the Fermi level lies close to the center of the apparent peak in the DOS, and based on relative changes in dark current it moves some 0.15 eV towards the band-edge over the aging period. This suggests the observed effects may be accounted for solely by changes in space-charge.

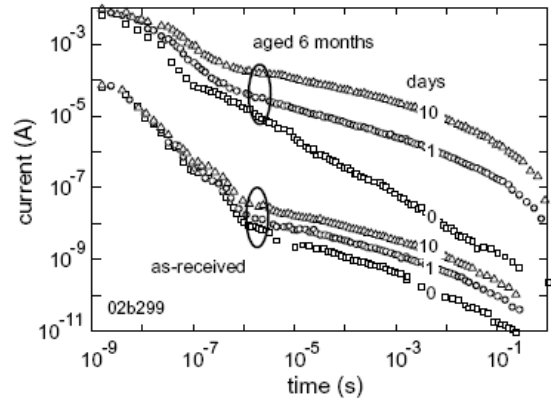


Fig. 4. Transient photocurrent decays for sample 02b299, in as-received condition and after aging for 6 months. Upper set of curves is offset in current by a factor of 100. Each set illustrates the effect of short-term aging, following annealing, over a 10-day period.

Fig. 5(b) shows that after 6 months a reduction of deeper defects (>0.45 eV), matched by an increase of shallower defects, has occurred. If this reflects a true change in the DOS, then the sample would re-equilibrate, giving a shift in Fermi level towards the conduction band edge. This interpretation is supported by a decrease in dark current activation energy (in the annealed state) from 0.55 to 0.48 eV and an increase in

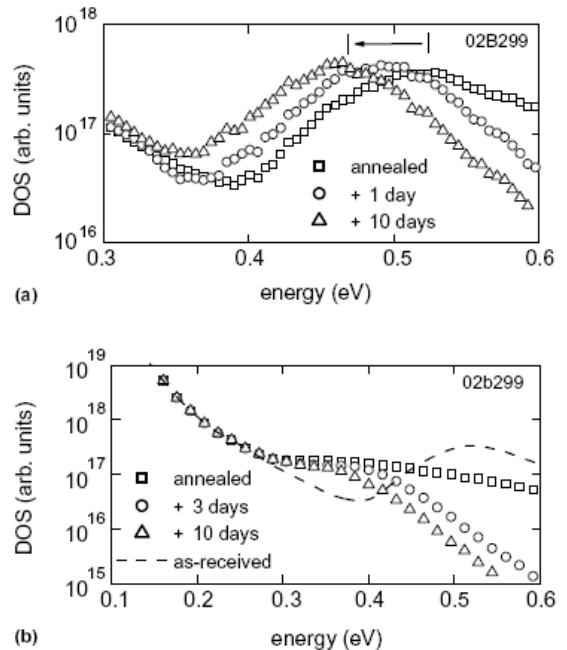


Fig. 5. DOS curves obtained from data shown in Fig. 4: (a) as-received, (b) after 6 months. An attempt-to-escape frequency of 10^{12} s^{-1} is assumed. Strictly speaking the DOS scale is uncalibrated, although the figures given may be taken as indicative relative to an assumed band-edge density of 4×10^{21} cm^{-3} eV^{-1} .

room temperature dark conductivity by a factor of approximately 10 over the 6-month period. Since it is widely believed that defects in microcrystalline silicon arise at grain boundaries, the long-term change in the DOS may indicate a permanent reconfiguration of dangling bonds, or barrier parameters, due to oxidation. The effects of the 10-day aging cycle are still reversible after 6 months and as before may be accounted for by electrostatic effects. DOS curves showing similar behaviour have previously been reported for films spanning a range of crystallinities and dark conductivities [10, 14].

As a check of the DOS extraction procedure, we have simulated the TPC decays using the DOS distributions for the as-received and 6-month aged sample in the annealed state. The simulation assumes multiple-trapping transport of electrons, with a fixed recombination time. It can be seen from Fig. 6 that there is good agreement over eight orders of magnitude of time.

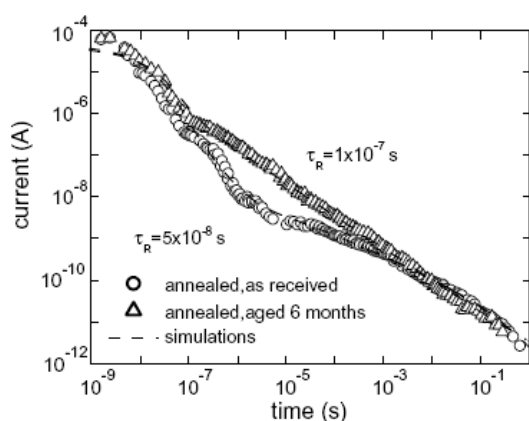


Fig. 6. Current–time decays simulated from DOS distributions shown in Fig. 5(b) for as-received and 6-month aged sample, following annealing.

4. Conclusions

Steady-state and transient photoconductivity measurements may be used successfully to study the electronic effects of exposure to room air on carrier transport in microcrystalline silicon films. Samples showing an increase in dark conductivity exhibit a short-term reversible effect and a longer-term permanent effect. The short-term effect causes a systematic increase in $\mu\tau$ -product and decrease in photoconductivity index, and changes in the occupancy of localized states attributed to reversible changes in space-charge due to water or oxygen adsorbed on the surface of the film, within cracks or at grain boundaries. The permanent effect is due to a change in the density of states distribution, accompanied by a small Fermi

level shift, in accordance with the observed increase in dark current and reduction in activation energy. It may originate from chemical modification of grain boundaries due to slow oxidation. Work extending the application of these techniques to a wider range of samples and ambient conditions is ongoing.

Acknowledgements

The authors thank A. Lambertz, S. Michel and T. Dylla of IPV Jülich for deposition and characterization of samples.

References

- [1] M. Tanielian, *Philos. Mag. B* 45 (1982) 435.
- [2] S. Veprek, Z. Iqbal, R.O. Kuhne, P. Capezzuto, F.-A. Sarott, J.K. Gimzewski, *J. Phys. C: Solid State Phys.* 16 (1983) 6241.
- [3] H. Fritzsche, in: J.I. Pankove (Ed.), *Semiconductors and Semimetals*, vol. 21, Part C, Academic, New York, 1984, Chapter 9.
- [4] F. Finger, R. Carius, T. Dylla, S. Klein, S. Okur, M. Gunes, *IEE Proc. CDS* 150 (2003) 300.
- [5] J. Meier, S. Dubail, J. Cuperus, U. Kroll, R. Platz, P. Torres, J.A. Anna Selvan, P. Pernet, N. Beck, N. Pellaton Vaucher, Ch. Hof, D. Fischer, H. Keppner, A. Shah, *J. Non Cryst. Solids* 227–230 (1998) 1250.
- [6] R. Bruggemann, A. Hierzenberger, H.N. Wanka, M.B. Schubert, *Mater. Res. Soc. Symp. Proc.* 507 (1999) 921.
- [7] S. Reynolds, C. Main, R. Bruggemann, *Mater. Res. Soc. Symp. Proc.* 762 (2003) A19.13.1.
- [8] O. Vetterl, F. Finger, R. Carius, P. Hapke, L. Houben, O. Kluth, A. Lambertz, A. Muck, B. Rech, H. Wagner, *Solar Energy Mater. Solar Cells* 62 (2000) 97.
- [9] S. Reynolds, C. Main, D.P. Webb, M.J. Rose, *Philos. Mag. B* 80 (2000) 547.
- [10] R. Bruggemann, *J. Mater. Sci. – Mater. El.* 14 (2003) 629.
- [11] R. Bruggemann, C. Main, *Phys. Rev. B* 57 (1998) R15080.
- [12] I. Solomon, M.H. Brodsky, *J. Appl. Phys.* 51 (1980) 4548.
- [13] C. Main, F. Dick, S. Reynolds, W. Gao, R.A.G. Gibson, *J. Non Cryst. Solids* 198–200 (1996) 263.
- [14] S. Reynolds, V. Smirnov, C. Main, R. Carius, F. Finger, *Mater. Res. Soc. Symp. Proc.* 715 (2002) A21.2.1.