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Metastable effects in silicon thin films: Atmospheric adsorption and light-induced degradation

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Abstract

The effects of exposure to atmosphere (ageing) and light-soaking on coplanar dark- and photo-conductivity of silicon films of varying crystallinity are examined. Dark conductivity generally increases on ageing in films with significant amorphous fraction and decreases in largely crystalline films, and may be reversed by annealing under vacuum at 130 °C consistent with adsorption and desorption of atmospheric components. Thinner films are more strongly affected by ageing. Boron doping appears to compensate charge introduced by ageing, though there are disagreements in detail. In comparison with ageing, moderate light-soaking affects dark conductivity in transitional microcrystalline silicon films only slightly. Both processes change the majority carrier mu–tau product in line with shifts in Fermi level position.

Keywords: Silicon; Solar cells; Conductivity; Microcrystallinity; Porosity; Nanocrystals; Adsorption

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1. Introduction

Amorphous and microcrystalline silicon films [1-4] and solar cells [5-7] have been shown to be sensitive to exposure to ambient atmosphere. In a previous study, Finger et al. [3] examined such effects in microcrystalline silicon in detail, and found correlations with film structure composition. To assist in a description of their behavior, they classified films into two groups: porous (so-called type I material), and compact (type II). Type I material is of high crystalline volume fraction, with large grain size and crystalline columns separated by deep cracks visible in TEM. Type II material is prepared under conditions closer to all-amorphous growth, with smaller grain sizes and distinguishable amorphous volume fractions. Defect densities as measured by ESR may exceed 10^{17} cm^{-3} in type I material, but may be as low as 10^{16} cm^{-3} in type II material.

Generally, coplanar dark conductivity in type I films decreases after storage in room air, but increases for type II materials. The original state may be recovered by annealing in vacuum or inert gas [3], though irreversible changes can also occur [4]. Wang et al. [7] have studied similar effects in amorphous silicon films and solar cells prepared using HWCVD, observing increase in dark conductivity and decrease of solar cell efficiency on storage in air. Changes in material and solar cell properties of microcrystalline silicon on exposure to light have also recently been reported [5,8,9].

Here, we present a comparative study of the effects of atmospheric exposure (or ageing) and light-soaking on silicon films of varying crystallinity, thickness and doping. Since exposure to atmosphere as well as to light may take place during solar cell fabrication and operation, it is important to isolate and quantify each effect.

2. Experimental

μc-Si:H films were deposited at IPV, Forschungszentrum Jülich by PECVD at 95 MHz onto borosilicate glass substrates at 200 °C at gas pressure 300 mTorr, silane concentration SC = $[SiH_4]/([SiH_4] + [H_2])$ between 3% and 7% and RF power 8 W [10]. Deposition rates were between 0.5 and 1.5 Å/s. The amorphous silicon film was deposited in a 27 MHz PECVD reactor, substrate temperature 200 °C, SC = 95%, gas pressure 500 mTorr. The Raman integrated intensity ratio $I_{CRS} = (I_{520} + I_{500})/(I_{520} + I_{500}$

+ I_{480}), where the subscripts refer to the wavenumber of the spectral peaks, was used to compare film morphology in terms of crystalline content [11]. For electrical measurements, 5 mm metal contacts separated by a 0.5 mm gap were deposited.

Dark conductivity (σ_D) and photo-conductivity were measured at 300 V dc bias using a Keithley 617 electrometer interfaced to a PC. A calibrated red LED was used as a light source. The compound error in conductivity measurements was typically 20%, dominated by sample geometry. Repeated ageing and light-soaking cycles were normally reproducible to within a factor of two for a batch of samples.

3. Results and discussion

Changes in σ_D observed on ageing and annealing for a series of silicon films are presented in Fig. 1(a). At low I_{CRS} and up to the transition from microcrystalline to amorphous growth, σ_D increases on ageing in room air, and may be reversed on annealing in vacuum. At higher I_{CRS} films show a reduction in σ_D on ageing. Irreversible longer-term ageing components [3, 4] are not considered here.

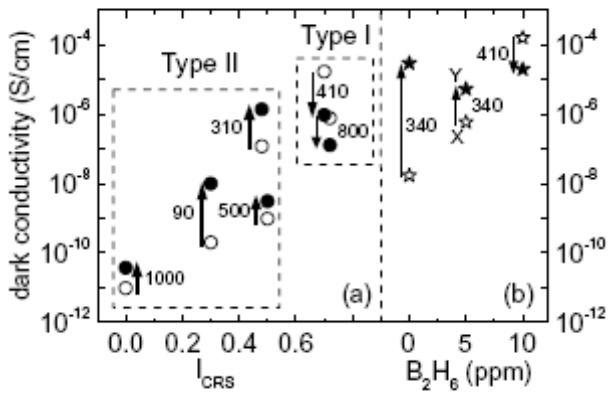

Fig. 1. Ageing behavior of microcrystalline silicon films versus (a) crystallinity, and (b) diborane concentration. Open symbols represent σ_D (300 K) following annealing at 160 °C under a vacuum of 10^{-3} Torr for 10 min. Filled symbols represent σ_D (300 K) after ageing in room air in the dark for typically seven days. Arrows emphasise direction of conductivity change. Numbers next to pairs of points denote film thickness in nm.

Boron doping may reduce or apparently reverse the direction of changes in σ_D due to ageing (Fig. 1(b)). The greatest relative effect is seen in the nominally undoped film (0 ppm diborane), where σ_D increases by some three orders of magnitude over seven days. At 5 vppm, the increase in σ_D after ageing is reduced by two orders of magnitude, to a factor of 10. At 10 vppm, a decrease in σ_D of about one order of magnitude occurs. Assuming constant surface charging or doping, the largest relative effect of ageing on σ_D would be anticipated when the Fermi level is in a low density of states, probably close to mid-gap. Activation energy measurements (not shown here) suggest this is the case for the 0 ppm sample. The 5 ppm sample is slightly p-type, and so the doping effect of ageing firstly compensates the boron doping and then renders the film n-type. This interpretation is supported by Fig. 2, which shows a *dip* in σ_D as ageing proceeds, expected if the Fermi level effectively traverses the band-gap. Similar behavior was reported by Tanielian [1] for p-type amorphous silicon films. The behavior of the 10 ppm film is, however, not entirely consistent. As the initial σ_D of this film is about 10^{-4} S/cm, and the final σ_D of the other two films is of order 10^{-5} S/cm, a reduction in σ_D due to 'compensation' of ageing by not more than 10% would be expected, yet a factor of 10 is observed, such that all three doped films have similar σ_D after ageing. Thus it seems that more subtle processes may also occur. It would be instructive to compare the behavior of an n-type series, but this has not yet been done.

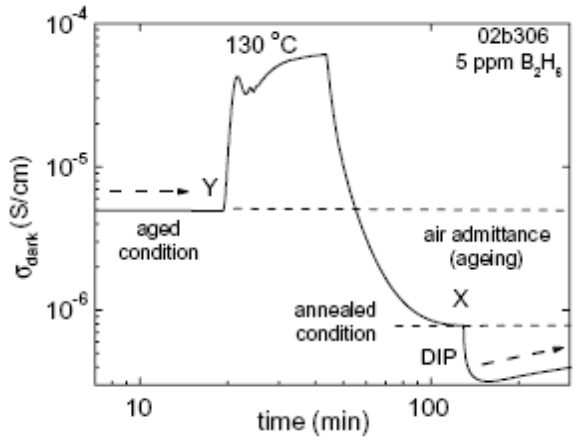

Fig. 2. Ageing/annealing cycle for sample doped with 5 vppm diborane, showing changes in conductivity versus time. Points X, Y link to the 5 vppm sample in Fig. 1.

Fig. 3 illustrates the dependence of σ_D on atmospheric adsorption versus film thickness. The ageing sensitivity is defined as the ratio of maximum to minimum steady σ_D values obtained following ageing and annealing. Both type I and type II behaviors are included. The trend supports the view that thinner films are more sensitive to the ageing process. This may be because a greater fraction of the film bulk is affected by surface adsorption, or to a

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more porous structure in the initial growth region [11,12]. In samples aged for several weeks it has been observed that even for thicker films, at least 50% of the total change in dark conductivity has taken place after two days. Thus we believe that the values given here, after seven days, are close to saturation. However it is possible that the greater rate at which ageing occurs in thinner films [13] may also contribute.

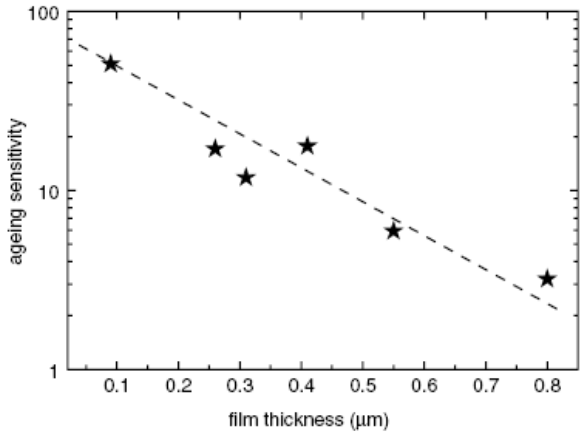

Fig. 3. Ratio of maximum to minimum conductivity following ageing and annealing versus film thickness, for various microcrystalline silicon films. Ageing and annealing regimes are as given in the legend to Fig. 1. The dashed line indicates the apparent trend of the data.

Fig. 4(a) presents the effects of both light-soaking and ageing on a film prepared at the transition from amorphous to microcrystalline growth (I_{CRS} = 0.48). The sample was firstly annealed in the dark (state 1, 10^{-7} S/cm). On exposure to room air for several days in the dark, σ_D increased (state 2, 1.5 × 10^{-6} S/cm). Following light-soaking under AM1 for 20 h at 50 °C [9], σ_D fell (state 3, 3 × 10^{-7} S/cm). Applying short heating pulses in vacuum (90–130 °C for 1 min.) reduced σ_D to a minimum value (state 4, 5 × 10^{-8} S/cm). Subsequent longer, higher temperature annealing (160 °C for 1 h) was found to increase σ_D (return to state 1). Steps 1–4 could be repeated through several cycles, with similar results. We believe the short, low-temperature annealing may remove adsorbed atmospheric components from the film, revealing σ_D of the light-soaked state, whereas more thorough annealing also removes light-induced defects. We could not confirm this simply by light-soaking an annealed sample under vacuum, because our vacuum base pressure (10^{-3} Torr) was insufficient to prevent some inadvertent ageing. The possibility that some light-induced defect species (see for example Biswas and Pan [14]) are removed by the low-temperature anneal cannot therefore be ruled out.

In keeping with earlier studies on amorphous [15, 16] and microcrystalline [17] silicon, Fig. 4(b) indicates that increases in mu–tau product and σ_D are linked by the upward shift in the Fermi level, as deeper-lying defect states become filled and no longer act as recombination centres.

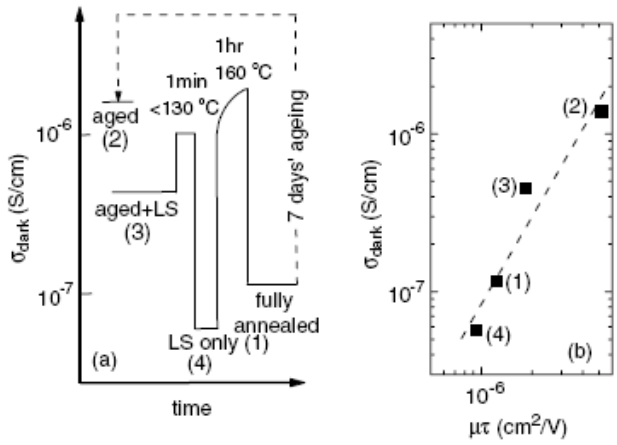

Fig. 4. Effects of ageing and light-soaking on microcrystalline silicon film (I_{CRS} = 0.48). (a) Changes in σ_D following ageing, light-soaking and annealing as described in the text; (b) relation between σ_D and mu–tau product of majority carriers, $\mu\tau = \sigma_{PC}/eG$, where photo-conductivity σ_{PC} was measured at 650 nm and flux G = 10^{14} cm^{-2} s^{-1}. All conductivity measurements were made at 300 K.

4. Conclusions

Microcrystalline silicon films may exhibit an increase or a decrease in conductivity on exposure to room air (ageing), that is correlated with film morphology, thickness and doping. The increase in conductivity appears to be associated with electron transport, as it may be 'compensated' by doping with boron. Ageing and light-soaking affect the majority carrier mu–tau product through shifts in Fermi level position. As changes in conductivity due to light-soaking may be relatively small in comparison to ageing, exposure to atmosphere during light-soaking/annealing experiments, or when samples are transferred between measurement systems etc., may need taken into account.

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