

Rapid Reversible Degradation of Silicon Thin Films by a Treatment in Water

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Metastability effects in amorphous and microcrystalline silicon thin films induced by exposure to atmospheric gases and water are investigated. A simple procedure is described which allows studying such effects in a reproducible and reliable manner on a short time scale. The method is applied to thin film silicon materials with different structure composition ranging from amorphous to highly crystalline. It is shown that the materials can be brought back into a well defined state even after pro-longed and repeated degradation cycles.

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Metastable effects in amorphous and microcrystalline silicon related to atmospheric gas adsorption or oxidation, are well known phenomena.¹⁻⁹⁾ However, a detailed model to explain or predict such changes depending on the material microstructure does not exist up to now. These effects have been investigated by various techniques, including conductivity measurements, IR spectroscopy,^{2,3)} transient and modulated photoconductivity (TPC and MPC),^{4,5)} steady state photocarrier grading (SSPG)⁶⁾ and electron spin resonance.³⁾ Reversible atmospheric-related degradation involves electrostatic adsorption of molecules causing a charge at the surface that is compensated by an accumulation of charge in the thin film. This results in band bending, which may influence the electronic transport.³⁻⁶⁾ Consequently, also changes in carrier lifetime⁶⁾ and apparent density of states,^{4,5)} as evaluated from SSPG, TPC, and MPC techniques, were found. Metastability effects are observed when the sample is exposed to ambient air on a timescale from several days³⁻⁶⁾ up to several weeks.⁷⁾ Among the several experimental methods, the dark conductivity is a simple-to-measure and quite sensitive parameter to monitor atmospheric-related changes and can be used to judge on the degree of material degradation.³⁻⁹⁾ Dark conductivity changes up to 3 orders of magnitude have been reported by several laboratories.³⁻⁹⁾ Both decrease and increase in dark conductivity, depending on the details of the materials structural composition and the experimental procedures have been found. However, the procedure for the degradation of samples in ambient air is usually not well controlled on a long timescale, since the humidity and temperature of the ambient air may differ with time and location. This complicates an adequate analysis of the results obtained from different techniques within a single laboratory and also complicates a comparison of the results from various groups, available in the literature. Additionally, the process of degradation of a sample in ambient air is time consuming and ranges from days to months³⁻⁹⁾ for different samples. Finally, it is desirable to determine a procedure which will enable us to measure the samples reproducibly in a well defined state.

In the present work we have developed a fast reversible and reliable degradation and recovery procedure, described in term of the changes in dark conductivity, using a series of thin silicon films prepared by hot wire (HW) and plasma enhanced chemical vapor deposition (PECVD). Samples, ranging from amorphous to highly crystalline, were degraded

in deionised water for varied times (up to 2 h) at room temperature and at 80 °C with an annealing recovery step at 160 °C. We see the need to provide an experiment which will enable us to investigate these effects reproducibly and on a short time scale. Only after such an experiment is available and confirmed to provide reliable data, we will be able to collect statistically relevant information on the variety of effects in the hydrogenated amorphous/microcrystalline silicon material with different structure compositions.

Undoped silicon thin films were deposited on glass substrates at a temperature around 200 °C by HW- and PECVD from a mixture of silane and hydrogen gases. The silane gas flow ratio $SC = [SiH_4]/([SiH_4] + [H_2])$ was varied between 2 and 12%. Details of the deposition conditions can be found elsewhere.^{7,10)} The thickness of the films was around 1 μm. Conductivity was measured with evaporated Ag contacts (5 mm in length, 0.5 mm gap). Raman spectra were measured with 647 nm excitation wavelength. The Raman intensities at 480 and 520 cm⁻¹ were used to estimate the crystalline fraction $I_{CRS} = I_{520}/(I_{520} + I_{480})$.¹¹⁾

Degradation of the samples was performed in a beaker in deionized (DI) water at room temperature or 80 °C for various periods of time up to 2 h. Annealing was performed under vacuum of 10⁻⁵ mbar for 30 min at 160 °C. Conductivity measurements were always done at 300 K under vacuum of 10⁻⁵ mbar after each degradation step and after annealing at 160 °C. Then the experimental cycle was repeated with the same conditions or at different degradation times or temperature.

Figure 1 shows the effects of degradation in DI water at temperature of 80 °C for 30 and 60 min on dark conductivity for a range of silicon thin films with I_{CRS} varied between 0 to 78%. The data are normalized to the initial conductivity values before degradation. The dark conductivity increases on degradation in water for the films with I_{CRS} below 60%. For the highly crystalline sample ($I_{CRS} = 78%$) dark conductivity decreases. Treatment in water for 30 and 60 min respectively results in very similar changes and annealing brings the sample back to the initial state before treatment. The observed direction of changes in conductivity upon exposure to water as a function of crystallinity and the recovery upon annealing are in agreement with previous observations.³⁻⁷⁾

Figure 2 summarizes the effects of degradation in water at 80 °C for 30 min versus the material crystallinity I_{CRS} for the series of samples investigated. The strongest effect is observed for amorphous films ($I_{CRS} = 0%$), where the dark

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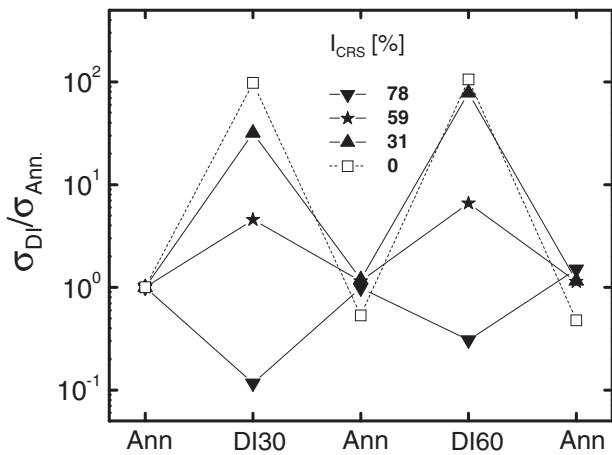


Fig. 1. Changes in dark conductivity for samples with different crystallinity I_{CRS} after cycles of degradation in water at a temperature of 80 °C for 30 and 60 min (DI30 and DI60, respectively) and annealing at 160 °C (Ann). The conductivity data are normalized to the value after the initial annealing step. The lines are to guide the eye.

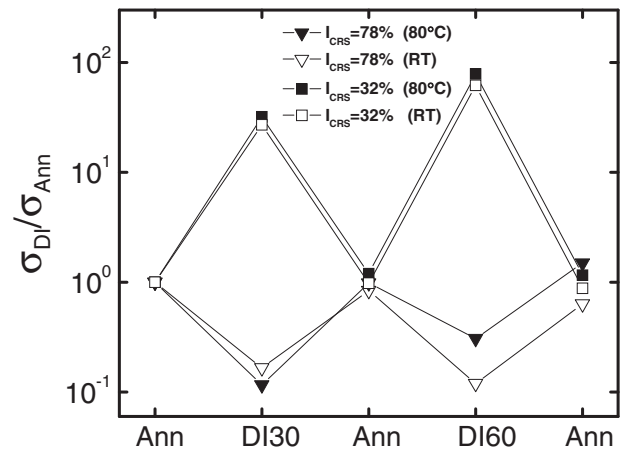


Fig. 3. Changes in dark conductivity for samples with medium and high crystallinity I_{CRS} after cycles of degradation in water at room temperature of about 20 °C and at 80 °C for 30 and 60 min. The conductivity data are normalized to the value after the initial annealing step. The lines are to guide the eye.

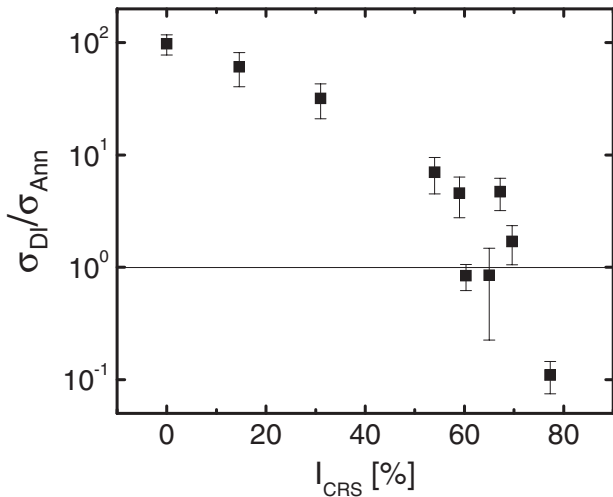


Fig. 2. Changes in dark conductivity upon degradation in water at a temperature of 80 °C for 30 min as a function of crystallinity I_{CRS} of the samples. A value of 1 (horizontal line) indicates no degradation. The conductivity data are normalized to the value after the initial annealing step.

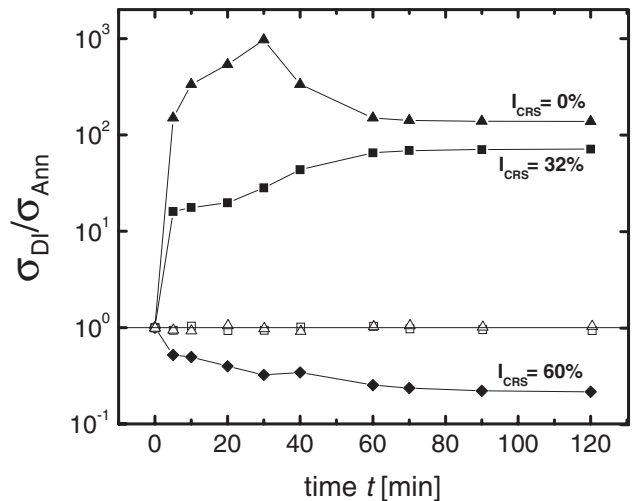


Fig. 4. Effect of degradation time on changes in dark conductivity of samples with different crystallinity after treatment in DI water at room temperature (20 °C). The conductivity data are normalized to the value after the initial annealing step. The lines are to guide the eye.

conductivity after degradation (σ_{DI}) increases by two orders of magnitude. The magnitude of change in conductivity decreases with increasing crystallinity. For the films with the highest crystallinity, the dark conductivity decreases after degradation. For an individual sample with medium crystallinity the direction of change, i.e., decrease or increase of the dark conductivity after degradation was found to change between the first and the second degradation cycle (large error bar in Fig. 2). The material with I_{CRS} around 60–70% shows the smallest degradation. This material is prepared under conditions which yield best performance when implemented into solar cells. From detailed material structure investigations it was found¹²⁾ that such “optimum phase mixture”¹³⁾ material is compact in a sense that regions between crystalline columns are filled with amorphous materials. One can imagine the crystalline columns to be covered with an amorphous skin.

To investigate the effect of temperature (room temperature of about 20 and 80 °C) during the degradation in water we have selected two samples with low and high I_{CRS} (32 and 78%, respectively). At each temperature the samples were exposed for 30 and 60 min. The results are shown in Fig. 3. The changes in conductivity are very similar for both temperatures (20 or 80 °C). Also the exposure time between 30 and 60 min seems to have no strong effect on the magnitude of change in conductivity. This was studied in more detail in the following.

Figure 4 shows the effects of degradation time t on dark conductivity for fully amorphous ($I_{CRS} = 0\%$), low crystallinity ($I_{CRS} = 32\%$) and highly crystalline ($I_{CRS} = 60\%$) samples. The degradation was performed in DI water at room temperature (≈ 20 °C). For $t < 60$ min, σ_{DI} varies with degradation time, while for degradation longer than 60 min σ_{DI} tends to saturate for all samples. Note that after each

degradation step in water, the dark conductivity can be restored upon annealing to the initial value with very good reproducibility even for samples with very low initial conductivity (open symbols in Fig. 4). It indicates that the degradation procedure applied here is fully reversible after annealing at 160 °C for 30 min. It was previously reported that irreversible degradation in thin silicon films, associated with oxidation at grain boundaries, may take place on a much longer time scales up to several months.^{3,4)} In the present set of experiments the samples were rapidly degraded, up to maximum time of 2 h. As a consequence only reversible metastable effects were found in our experiments while for longer exposure times (or alternatively exposure at higher temperature or in pure oxygen atmosphere) also non-reversible effects are found.³⁾

In summary, we have studied metastability effects in thin films of amorphous and microcrystalline silicon, prepared by HWCVD and PECVD. Using a cycle of exposure to water and subsequent annealing at 160 °C, a rapid, reproducible and reversible change in the dark conductivity can be provoked. The magnitude and direction of change in conductivity, i.e., higher or lower conductivity, depends on the material's crystallinity in agreement with earlier studies. Exposure temperatures of about 20 and 80 °C result in very similar changes in conductivity, thus the degradation procedure can be conveniently maintained at room temperature without need of heating. The magnitude of change increases with exposure time initially but tends to saturate for exposure times longer than 60 min. After annealing at 160 °C the initial value of conductivity is fully restored even after prolonged and repeated exposure cycles. The described

procedure of degradation in deionized water can be used as a reproducible and rapid method when reversible metastable effects in silicon thin films are investigated.

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- 1) M. Tanielian: *Philos. Mag. B* **45** (1982) 435.
 - 2) S. Veprek, Z. Iqbal, R. O. Kuhne, P. Capezzuto, F.-A. Sarott, and J. K. Gimzewski: *J. Phys. C* **16** (1983) 6241.
 - 3) F. Finger, R. Carius, T. Dylla, S. Klein, S. Okur, and M. Günes: *IEE Proc.—Circuits Devices Syst.* **150** (2003) 300.
 - 4) V. Smirnov, S. Reynolds, C. Main, F. Finger, and R. Carius: *J. Non-Cryst. Solids* **338–340** (2004) 421.
 - 5) R. Brüggemann, C. Longeaud, and J. P. Kleider: *MRS Symp. Proc.* **808** (2004) A9.8.
 - 6) N. Souffi, G. H. Bauer, and R. Brüggemann: *Thin Solid Films* **501** (2006) 129.
 - 7) V. Smirnov, S. Reynolds, F. Finger, R. Carius, and C. Main: *J. Non-Cryst. Solids* **352** (2006) 1075.
 - 8) M. Sendova-Vassileva, S. Klein, and F. Finger: *Thin Solid Films* **501** (2006) 252.
 - 9) G. Yilmaz, E. Turan, M. Günes, V. Smirnov, F. Finger, and R. Brüggemann: *Phys. Status Solidi C* **7** (2010) 700.
 - 10) T. Chen, Y. Huang, D. Yang, R. Carius, and F. Finger: *Phys. Status Solidi: Rapid Res. Lett.* **4** (2010) 61.
 - 11) L. Houben, M. Luysberg, P. Hapke, R. Carius, F. Finger, and H. Wagner: *Philos. Mag. A* **77** (1998) 1447.
 - 12) F. Finger: in *Thin-Film Silicon Solar Cells*, ed. A. V. Shah (EPFL Press, Lausanne, 2010) Chap. 3, p. 97.
 - 13) Y. Mai, S. Klein, R. Carius, J. Wolff, A. Lambertz, F. Finger, and X. Geng: *J. Appl. Phys.* **97** (2005) 114913.