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ARTICLE

Investigation of meta- and in-stability effects in hydrogenated microcrystalline silicon thin films by the steady-state measurement methods[1]

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Abstract: Metastability effects because of atmospheric exposure, high purity gasses, and deionized water in hydrogenated microcrystalline silicon thin films with different crystalline volume fractions were studied using well accepted steady-state characterization methods of dark conductivity, steady-state photoconductivity, steady-state photocarrier grating (SSPG) and dual beam photoconductivity (DBP) methods. A standard measurement procedure has been established before using the steady state methods, in which a steady state condition of dark conductivity was established by monitoring the time dependence of dark conductivity. Samples deposited on smooth glass and rough glass substrates exhibit similar reversible and irreversible changes in the properties of microcrystalline silicon film. A reliable correlation of reversible and irreversible changes indicate that dark conductivity and photoconductivity values increase, sub-bandgap absorption spectrum obtained from DBP method decrease and correspondingly minority carrier diffusion lengths obtained from the SSPG method increase in the metastable state in various amount for microcrystalline films with crystalline volume fraction, $I_C^{RS} > 0.30$. Amorphous silicon and microcrystalline silicon films with $I_C^{RS} < 0.30$ do not show detectable metastable changes as samples exposed to atmospheric condition as well as high purity oxygen gas and deionized water.

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Résumé : Nous utilisons des méthodes de caractérisation stationnaire bien acceptées, comme la conductivité en obscurité, la photoconductivité stationnaire, la photoconductivité stationnaire par interférométrie laser (SSPG) et la photoconductivité modulée à deux faisceaux (DBP), afin d'étudier l'effet de la métastabilité dans des films minces de silicium microcristallin hydrogénés, suite à l'exposition à l'atmosphère, aux gaz de haute pureté et à l'eau dé-ionisé. Avant d'utiliser ces méthodes stationnaires, nous avons développé une procédure standard de mesure, dans laquelle la condition stationnaire de conductivité en obscurité est vérifiée en observant la dépendance en temps de la conductivité en obscurité. Les échantillons déposés sur des surfaces douces et rudes de substrats de verre montrent les mêmes changements réversibles et irréversibles dans les propriétés microcristallines des films de silicium. Une corrélation fiable des changements réversibles et irréversibles des propriétés des films microcristallins indique que les valeurs de conductivité en obscurité et de photoconductivité augmentent et que le spectre d'absorption sous la bande interdite obtenu de SSPG augmente dans les films microcristallins en état métastable pour lesquels la fraction cristalline en volume $I_C^{RS} > 0.3$. Les films de silicium amorphes et microcristallins avec $I_C^{RS} < 0.3$ ne montrent aucun changement métastable détectable lorsque les échantillons sont exposés aux conditions atmosphériques, à l'oxygène pur et à l'eau dé-ionisée. [Traduit par la Rédaction]

1. Introduction

Upon exposure of microcrystalline silicon (μc-Si:H) thin films to room ambient, water vapour, deonized water, or to different gas atmospheres, these materials frequently show reversible (metastability) and irreversible (instability) changes of their electronic properties. Even though the first published results appeared at the beginning of 1980s by Veprek et al. [1], more extensive investigation has been carried out in the last decade by using the methods, which probe the changes in a material parameter measured at the steady-state condition [1–6]. In most of those studies, highly conductive thin samples deposited on smooth glass substrate were used in measurements because of adhesion problems of thicker samples on the smooth glass substrates. Alternatively, rough glass substrates were used to investigate the metastability effect on thicker films [6], on which optical methods cannot be applied reliably. Because of the absence of light induced degradation in microcrystalline silicon, it has an advantage to use such thick intrinsic absorber layers for the development of μc-Si:H solar cell technology [7].

It was reported initially that conductivities in highly crystalline porous materials (called type I) decreased by a few orders, while compact materials (called type II) with significant amorphous fraction showed an opposite behaviour as samples exposed to room ambient [2]. In the later reports, the direction and magnitude of reversible conductivity changes in the metastable state show random variations [3-6] having no clear functional dependence on the crystallinity of the material because of missing well established standard measurement procedures among laboratories.

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Metastability known as the Staebler–Wronski effect because of light soaking in amorphous silicon films [8] is reversible after annealing and correlates very well with photoconductivity decrease and corresponding defect creation as detected by electron spin resonance (ESR) and sub-bandgap absorption methods [9]. However, such correlations between photoconductivity changes (decrease or increase) and defect creation (if any) because of atmospheric exposures is not well understood in microcrystalline silicon films yet. ESR studies for the air or oxygen exposed samples at 80 °C indicated an irreversible increase in ESR spin density for a resonance signal with an ESR *g*-value around $g = 2.0052$ in highly crystalline materials ($I_C^{RS} > 0.80$). In more compact materials (generally with crystalline volume fraction $I_C^{RS} < 0.70$) as well as in pure amorphous silicon films [10], much less effect on the ESR properties were observed. On the other hand, ESR signal contributions at around *g*-values of $g = 2.0043$ were only little affected by the described air or oxygen exposure. Although the microscopic identification and the energy distribution of these paramagnetic defects in the bandgap of microcrystalline silicon are still a matter of debate [10–12], speculatively they have been related to states in different structure environments, that is, in the material bulk or on grain boundaries or internal surfaces, and therefore with different susceptibility to exposure to air or water. However, these defects, depending on energy position and charge state will have a strong influence on the generation and recombination kinetics of majority and minority carriers as probed by the steady-state photoconductivity (SSPC) and steady-state photocarrier grating (SSPG) methods. It was shown that majority carrier $\mu\tau$-products can be affected by the air exposure and heat treatment of the samples, accompanying the corresponding changes in σ_{dark} while the minority carrier $\mu\tau$-products obtained from the SSPG measurements were found to be insensitive to the changes in σ_{dark}, suggesting such changes occurred only due to Fermi level shift obeying to the Meyer-Neldel rule [5]. It was recently reported that pure oxygen and deionized (DI) water treatment increased σ_{dark} and σ_{photo} irreversibly by a few orders [13]. These changes correlate well with permanent shift of dark Fermi level towards the conduction band edge, which will eventually increase the density of occupied defect states below the Fermi level. However, sub-bandgap absorption coefficient, $\alpha(h\nu)$, spectrum obtained by dual beam photoconductivity (DBP) method showed an opposite behaviour, a significant decrease in the low energy region of $\alpha(h\nu)$ indicating a decrease in the density of occupied defect states due to oxygen and deionized (DI) water exposure of μc-Si:H [13]. In this study, four different steady-state methods have been used on the same sets of samples under the same measurement conditions to understand the effects of reversible and irreversible changes due to air, oxygen and deionized water on the majority and minority carrier transport properties in undoped intrinsic microcrystalline silicon films.

2. Experimental details

We have developed a new standard measurement procedures and applied to investigate the metastability and instability phenomena in μc-Si:H thin films with a wide range of structure compositions using temperature dependent dark conductivity, steady-state photoconductivity, sub-bandgap absorption spectroscopy as detected by dual beam photoconductivity (DBP) and steady-state photocarrier grating (SSPG) methods. Measurement procedure is based on recording time dependence of dark conductivity as sample is in air, in exposing gas ambient, in vacuum, as well as during the annealing process before applying the steady-state measurement methods under light. SSPC, DBP, and SSPG measurements were performed as σ_{dark} remained unchanged with time. The percent change in σ_{dark}, $\Delta\sigma_{dark}$ ([$\Delta\sigma_{dark}$ = (σ_{dark}(measurement begins) – σ_{dark}(measurement ends))/σ_{dark}(measurement begins)]*100%) during the several hours of measurements was within less than 10%. DBP and SSPG systems have separate dedicated cryostat systems, in which both σ_{dark} and σ_{photo} are measured independently to confirm the same state of sample under investigation. Samples were exchanged between systems to characterize the same annealed and exposed states of the samples.

μc-Si:H films were deposited using VHF-PECVD at 190 °C on both smooth and rough glass substrates with low deposition rates. The microstructure of the films was changed from amorphous (a-Si:H) to highly crystalline by adjusting the process gas silane concentration during deposition. The crystallinity was evaluated from Raman measurements. Thickness of the samples varies between 200 and 1100 nm. Adhesion of thick silicon films on smooth glass substrate was succeeded using a very thin SiO_x interlayer coated on the smooth glass before silicon deposition. Silver coplanar electrodes were evaporated on the samples with 0.5 cm length and 0.5 mm separation. Collimated He–Ne laser light source was used to record SSPC measurements under Ohmic dc bias. SSPG measurements were carried out using He–Ne laser with flux ranging from 4×10^{16} to 2×10^{17} $cm^{-2}s^{-1}$ with an applied dc bias in the Ohmic and low field region, where only diffusion controlled transport dominates. The samples were randomly exposed to atmospheric gases by keeping them in the dark laboratory atmosphere. In addition, high purity oxygen gas treatment was performed in high vacuum cryostat at 80 °C. In addition, deionized water at 80 °C was used for faster and effective creation of reversible and irreversible changes in samples deposited on rough glass [14]. Annealing was carried out at 430 K in high vacuum of 2–3 × 10^{-6} mbar. All probe measurements were performed at 300 K in exposing gas ambient as well as in vacuum as sample is at the steady-state condition of dark conductivity.

3. Results and discussion

3.1. The effects of oxygen exposure

Conductivity of microcrystalline silicon films strongly depends on the sample history and the ambient in which sample is measured [5]. Therefore, monitoring σ_{dark} of the sample in different exposing and measurement ambient is crucial for the reliable correlation of results obtained from different techniques. In Fig. 1, time dependence of σ_{dark} for a microcrystalline silicon sample is presented for different measurement conditions. Long term air exposed sample was placed in cryostat and vacuum started. At the end of 20 h, σ_{dark} reached to a constant level (curve 1), where SSPC, DBP, and SSPG measurements were performed for the air exposed state. After measuring σ_{dark}, σ_{photo}, and minority carrier diffusion length, L_D, of air exposed state in SSPG system, the sample was heated up to 160 °C and annealed in vacuum until σ_{dark} becomes constant. Temperature dependence σ_{dark} was recorded as sample cooled to 300 K, called as "annealed1a" state as shown in Fig. 2. At 300 K, time dependence of σ_{dark} was also recorded in the annealed1a state for several hours and no significant change was detected. After completing SSPC and SSPG measurements of annealed1a state, sample was placed in DBP system and reannealed in vacuum again, called the "annealed1b" state in Fig. 2. It is seen that annealed1 states (a and b) obtained in both systems after air exposed state of sample are almost identical within 10% experimental error. Activation energy of σ_{dark} was calculated to be 0.49 eV. σ_{dark} at 300 K increased by 50% after the annealing process. σ_{photo} results measured in both systems for the same annealed1 state are shown in Fig. 3. It is seen that the results are on top of each other, confirming that the same state of sample was characterized in DBP and SSPG systems.

After characterizing the annealed1 state in vacuum, the pump valve was closed and high purity oxygen was purged in the cryostat. The sample was heated to 80 °C to increase the efficiency of oxygen-induced changes as reported previously [2]. Time dependence of σ_{dark} at 353 K was recorded during oxygen exposure of the sample. At the end of 8000 min, sample was cooled to 300 K in

Fig. 1. Time dependence of dark conductivity for 1.1 μm thick microcrystalline silicon with I_C^{RS} = 0.69 for different experimental conditions: (1) air exposed sample measured in vacuum (same for both DBP and SSPG systems); (2) oxygen exposed sample measured at 300 K in O_2 ambient in DBP system; (3) oxygen exposed sample at 300 K transferred to SSPG system and measured in O_2 ambient; (4) oxygen exposed sample measured at 300 K in vacuum in SSPG system; and (5) oxygen exposed sample transferred to DBP system and measured at 300 K in vacuum.

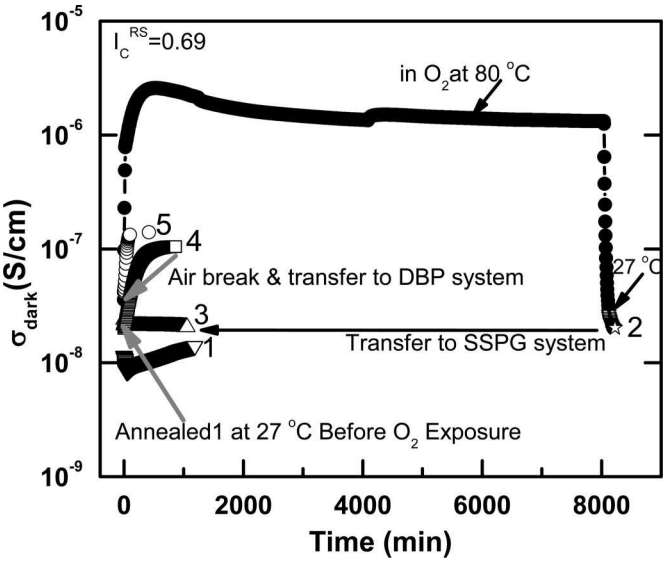
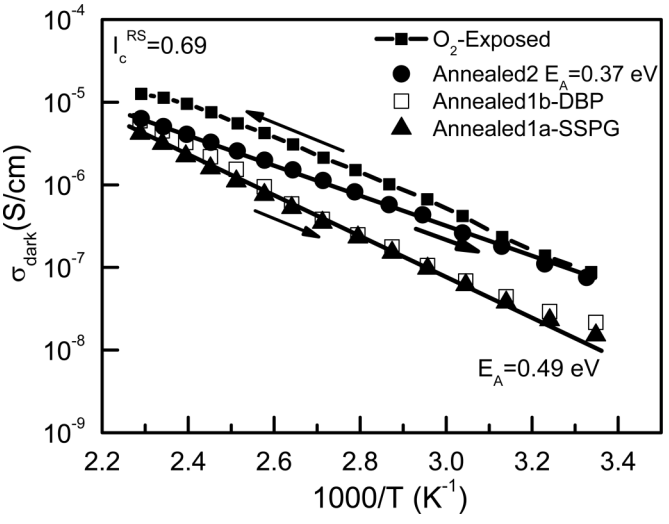
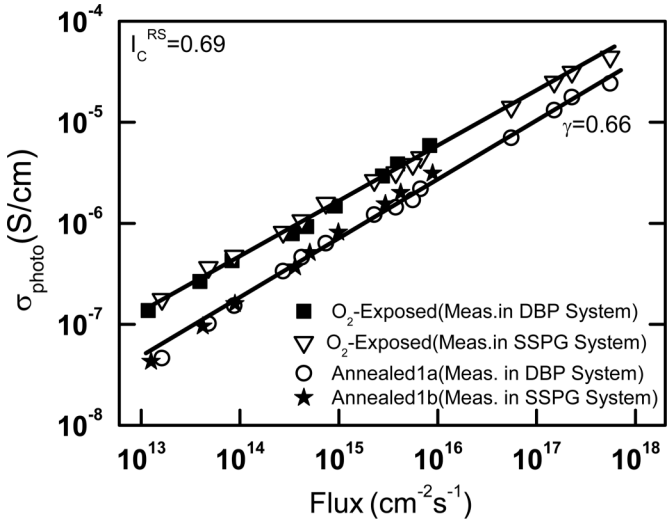


Fig. 2. Arrhenius plot of dark conductivity for 1.1 μm thick microcrystalline silicon with I_C^{RS} = 0.69 before and after oxygen exposure. Annealed1 states carried out before oxygen treatment were measured in DBP and SSPG systems separately.



oxygen ambient and waited until σ_{dark} reached to a constant level within less than 10% change. σ_{dark} measured in O_2 ambient was found to be very close to that measured in the annealed1 state taken before oxygen exposure as shown in Fig. 1. After characterizing the sample in DBP system in O_2 ambient, the sample was transferred to SSPG system and oxygen was purged in the cryostat and time dependence of σ_{dark} was recorded (curve 3) again. Almost identical σ_{dark} values in O_2 ambient were obtained in DBP and SSPG systems. SSPC results were also identical (data not shown

Fig. 3. Steady-state photoconductivity versus flux results for 1.1 μm thick microcrystalline silicon with I_C^{RS} = 0.69 in the annealed1 and oxygen exposed states. Measurement carried out for the same state of sample in SSPG and DBP systems are presented with different symbols. Measurements were performed in vacuum.



for clarity) and no change was obtained from the annealed1 state values shown in Fig. 3. When oxygen was pumped out in SSPG system, σ_{dark} starts to increase slowly and reaches a constant level at the end of 15 h pumping (curve 4) as shown in Fig. 1. Such change in σ_{dark} is likely not because of establishment of vacuum because the pressure of cryostats reaches the value of 2–3 × 10^{-6} mbar only after approximately 90 min and sample stays in such high vacuum during dark conductivity changes. Such observation was previously reported by Brueggemann that more than 100 h was needed to reach a constant level of σ_{dark} [5]. Oxygen exposed state measured in vacuum caused an increase in σ_{dark} by a factor of five. After performing SSPC and SSPG measurements, the oxygen exposed sample was transferred to DBP system (within 20 min of time in open air) and pumped again. Time dependence of σ_{dark} was recorded (curve 5) as shown in Fig. 1. At the end of 7 h vacuum process, σ_{dark} reached to a constant level, which is 50% higher than previous conductivity level obtained in SSPG system. Steady-state photoconductivity values increased by factor of two and almost identical results were measured in DBP and SSPG systems for the oxygen exposed state measured in high vacuum as shown with different symbols in Fig. 3. The function of vacuum after oxygen treatment is not well understood at the moment but a similar effect has been observed in all oxygen exposed samples with significant crystalline volume fractions investigated in this work. Such observation indicates the importance of measurement conditions for the characterization of metastability and instability effects as well as comparison of different results obtained with different methods in different laboratories. After detailed characterization of oxygen exposed state in vacuum, sample was heated to 160 °C and annealed for 16 h. Arrhenius plot of σ_{dark} for the "annealed2" state is presented in Fig. 2. σ_{dark}(300 K) increased almost by a factor of five irreversibly from the annealed1 state value. Activation energy decreased to 0.37 eV, indicating a permanent shift of the Fermi level because of charging of defect on the surface of grains caused by the permanent bonding of oxygen on the surface of grains [3].

The results of σ_{dark} and σ_{photo} presented earlier indicated that the same annealed and exposed states were recorded in DBP and SSPG systems. Therefore, additional information about metastable defect creation or passivation, if any, and their effects on the

Fig. 4. Relative sub-bandgap absorption spectra obtained from the DBP measurements under the lowest dc bias light condition for 1.1 μm thick microcrystalline silicon with I_C^{RS} = 0.69 in the air exposed, annealed1, oxygen exposed and annealed2 states. Measurements were carried out in high vacuum and were normalized at high energy part of the spectrum.

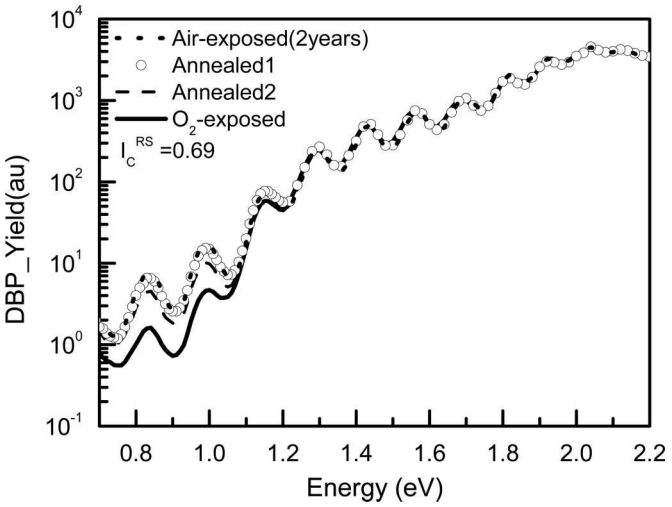
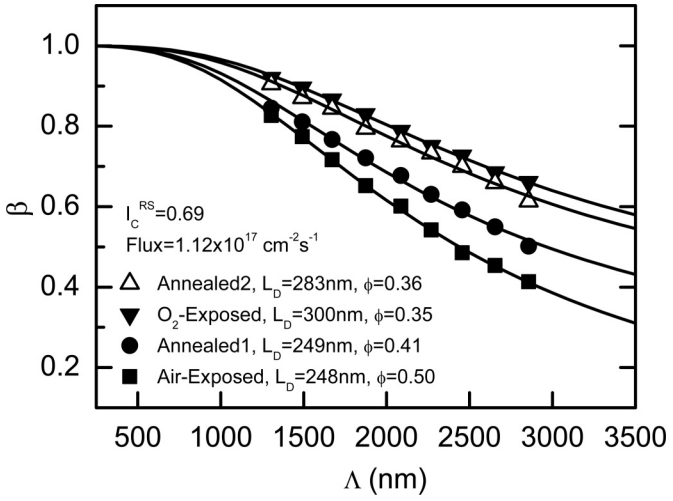


Fig. 5. Experimental β versus grating period Λ (symbols) results obtained from the SSPG measurements for 1.1 μm thick microcrystalline silicon with I_C^{RS} = 0.69 in the air exposed, annealed1, oxygen exposed and annealed2 states. Measurements were carried out in high vacuum. Lines are fits to data.



minority carrier diffusion lengths can be obtained using DBP and SSPG results. In Fig. 4, relative DBP yield spectra measured under the lowest dc bias light condition are shown for the same sample in the metastable and annealed states defined above. There is no significant change in DBP spectra of air exposed and annealed1 states. In addition, DBP spectrum for the oxygen exposed state measured in O_2 ambient was also identical (data not shown for clarity). However, oxygen exposed state measured in high vacuum resulted in a significant decrease in the DBP spectrum at the sub-bandgap energies as presented in Fig. 4. Because the DBP spectrum is very sensitive to the occupation of defect distribution in the bandgap (achieved by changing the dc bias light intensity), it is evident that the density of occupied defect states below the Fermi level decreases after oxygen exposure and following vacuum treatment. After the second annealing procedure, DBP spectrum recovers partially towards the level of the annealed1 state. Partial irreversible effect also exists in the defect absorption part of spectrum.

The effect of oxygen exposure on the minority carrier transport properties as detected by SSPG measurements is presented in Fig. 5 for the same sample at the same experimental conditions explained earlier. Minority carrier diffusion length, L_D, obtained from nonlinear fits to SSPG equation [15] between β versus grating period Λ is 250 ± 3 nm for air exposed and annealed1 states. It increases to 300 nm in the oxygen exposed state and partially recovers to 283 nm after the annealed2 state. An irreversible effect is also detected in SSPG measurements same as found for σ_{dark}, σ_{photo}, and DBP measurements. The most important point is that improvement of minority carrier diffusion lengths in the oxygen exposed state will result in an increase in hole $\mu\tau$-products, which can be possible only if the density of recombination centers for holes decreases below the Fermi level. Such confirmation was provided by the results of the sub-bandgap absorption spectra presented in Fig. 4.

3.2. The effects of deionized (DI) water treatment

It was reported that oxygen and DI water cause similar reversible and irreversible changes in microcrystalline silicon films with significant crystalline volume fractions [13]. We have used the samples deposited on rough glass substrate prepared under identical deposition conditions to investigate the reversible and irreversible changes because of DI water treatment. In Fig. 6, time dependent dark conductivity of 360 nm thick sample with I_C^{RS} = 0.70 is shown for air exposed, annealed1 and DI water treated states. σ_{dark} at 300 K remains constant for the annealed1 state. However, it shows different time dependence for air exposed and DI water treated states measured in air ambient and in high vacuum. Measurements in vacuum are similar to that of oxygen exposed state where dark conductivity slowly increases in vacuum until a constant value is reached. In addition, an effect of vacuum in DBP system results in even higher dark conductivity and photoconductivity values, similar to what observed and presented in Fig. 1 for oxygen exposed state for the sample deposited on smooth glass. Therefore, it seems that the treatments of the sample in oxygen and DI water result in similar changes in the properties of material. Apparently, 2 h of DI water treatment is more effective and causes larger increase in σ_{dark} and σ_{photo} than several hundred hours of oxygen gas exposure. Corresponding steady-state photoconductivity results are shown in Fig. 7 for the same measurement conditions. There is more than two orders of magnitude increase in σ_{photo} after DI water treatment and following vacuum process. In addition, the exponent γ changes from 0.70 in the annealed1 state to 0.50 after DI water treatment. These changes in conductivities cannot be recovered by the following 12 h annealing process carried out at 160 °C and mostly irreversible as seen in Fig. 7. This irreversible change is the instability effect. Activation energy of σ_{dark} measured in both DBP and SSPG systems resulted in identical value of 0.52 eV before the treatment. It decreased to 0.17 eV after the second annealing process carried out after DI water treatment, indicating a permanent shift of the Fermi level towards the conduction band edge because of surface charge created by the chemical bonding of oxygen on the surface of grains.

The results of samples deposited on the rough glass substrate obtained using the photoconductivity techniques may be influenced by the back reflection of light at the film–substrate interface. Because of light enhancement, direct comparison of results of samples deposited on smooth and rough glass substrates cannot be achieved successfully. However, a relative comparison of reversible and irreversible changes because of most effective DI water treatment can help understanding of the phenomena.

Fig. 6. Time dependent dark conductivity for a microcrystalline silicon film with I_C^{RS} = 0.70 deposited on rough glass substrate in the annealed1 state, in air after DI water treatment as well as in vacuum after DI water treatment measured in DBP and SSPG system.

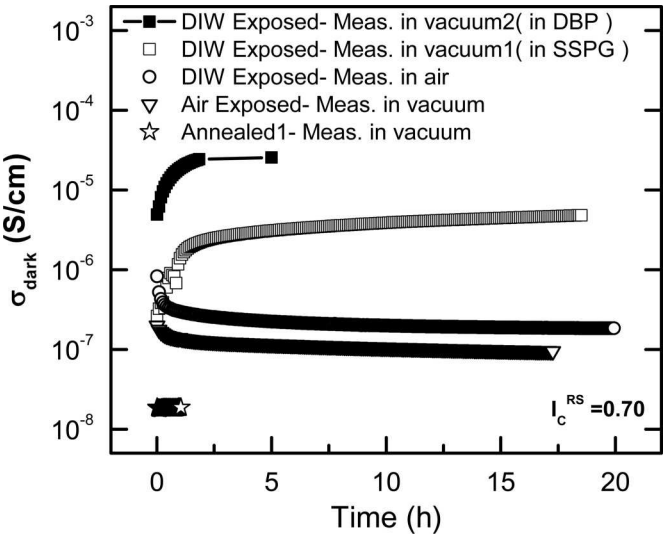
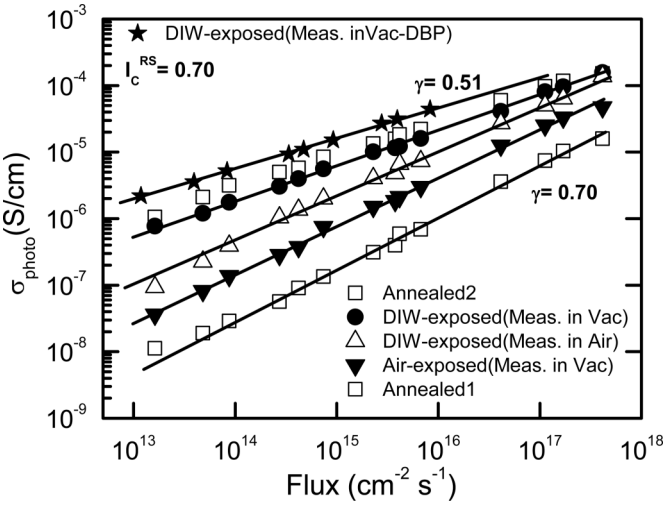
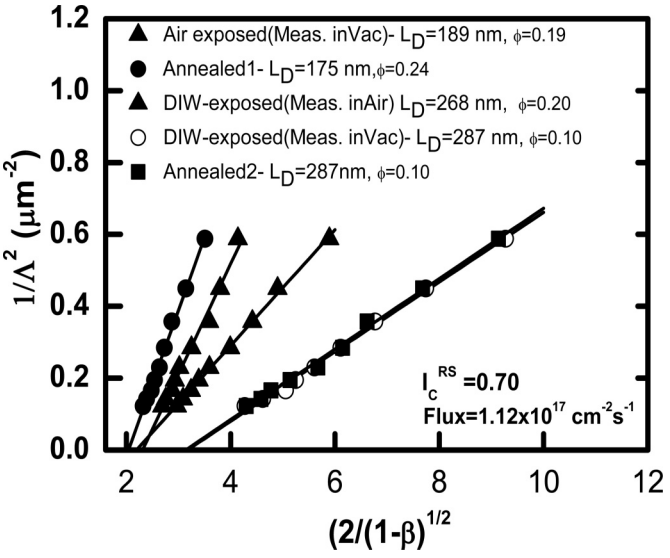


Fig. 7. Steady-state photoconductivity versus flux for a microcrystalline silicon film with I_C^{RS} = 0.70 deposited on rough glass substrate after air exposed, DI water exposed and annealed states.



SSPG measurements of the same sample on the rough glass are presented in Fig. 8 using linear Balberg plots [16] between experimental β and grating period Λ for air exposed, DI water exposed and annealed states. Minority carrier diffusion length, L_D, obtained from the fits to experimental data are strongly affected by DI water treatment similar to what has been observed after oxygen treatment and following vacuum process. The only difference for the rough samples is that the grating quality parameter ϕ decreased to 0.1–0.2 levels because of increased optical scattering as reported previously [6, 17]. L_D was found to be 189 nm in the air exposed state and decreased to 175 nm in the annealed1 state. It increased to 268 nm after DI water treated state measured in air ambient and further increased to 287 nm as sample measured in high vacuum, same as found for σ_{dark} and σ_{photo}. Final annealing process carried out in vacuum did not change the L_D value, which becomes irreversible, similar to what observed for σ_{dark} and σ_{photo}

Fig. 8. Linear plots for the SSPG results for a microcrystalline silicon film with I_C^{RS} = 0.70 deposited on rough glass substrate after air exposed, DI water exposed and annealed states.



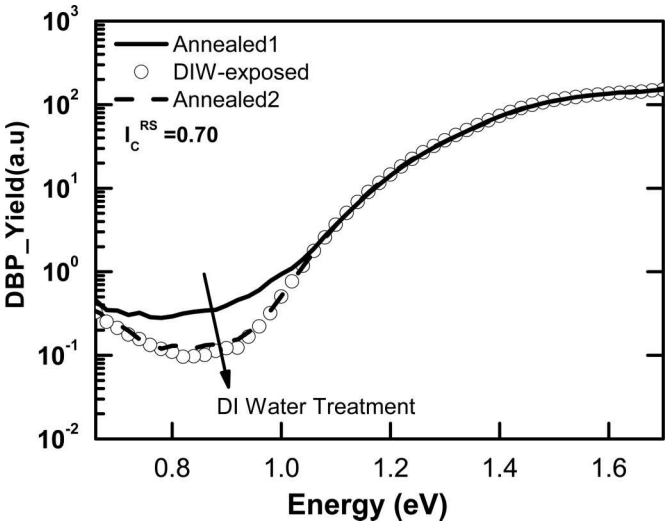
results presented earlier. Almost 65% improvement of minority carrier diffusion lengths results in an increase in the minority carrier hole μτ-products because of decreased density of recombination centers below the midgap. In Fig. 9, relative DBP yield spectra measured under the lowest dc bias intensity were presented for DI water exposed state and annealed states performed before and after the treatment to see any signs of changes in the occupation of defect states located below the Fermi level. It is clearly seen that DBP yield spectrum for DI water exposed state measured in vacuum significantly decreases in the low energy part of spectrum and becomes almost irreversible after annealed2 state, consistent with the results of σ_{dark}, σ_{photo}, and L_D obtained under the same experimental conditions.

These results obtained on μc-Si:H films with similar crystallinity deposited on smooth and rough glass indicate that several steady state photoconductivity methods can reliably be used to understand the mechanisms of metastability and instablity effects because of oxygen and water exposure. Both exposing ambients cause similar changes in conductivities, ambipolar diffusion lengths, as well as in sub-bandgap absorption coefficient spectra. These changes are mostly irreversible meaning the oxygen and water create more instability in the μc-Si:H films. Smaller metastable changes also exist, which are reversible after annealing. The irreversible changes in thick μc-Si:H films because of oxygen are rather small compared to those that occurred in thin sample created by DI water treatment, which could indicate that the penetration depth of oxygen in thick bulk material is rather small. It was also reported that changes in dark conductivity after air exposure decreases as samples get thicker [4]. Similar investigations were also performed on thick μc-Si:H films deposited on the smooth glass as well as those deposited on rough glass substrates with varying crystalline volume fractions. Even though results obtained on those materials were not presented here, the details can be found elsewhere [18]. It was found that reversible and irreversible changes in the measured parameters of amorphous and μc-Si:H films with I_C^{RS} < 0.30 is very little and no significant change can be recorded as consistent with previous investigations [10, 13].

4. Conclusion

We have established a new standard measurement procedure for the dark conductivity of microcrystalline silicon samples be-

Fig. 9. Relative DBP spectra measured under the lowest dc bias intensity for a microcrystalline silicon film with I_C^{RS} = 0.70 deposited on rough glass substrate for DI water exposed and annealed states measured in vacuum.



fore applying the other steady-state measurement techniques for the reliable investigation of metastability and instability effects caused by air, oxygen, and DI water treatment. It was found that oxygen exposure and DI water treatment cause similar reversible and irreversible changes in measured parameters of the films, but DI water treatment is faster and more effective. Thicker samples are less affected by the oxygen exposure while thin samples show a few orders of magnitude increase in conductivities. Such irreversible increase in σ_{dark} and σ_{photo} can be explained by the Fermi level shift towards the conduction band edge because of space charge created by the oxygen chemically bonded to the surface of grains. The changes in minority carrier diffusion lengths, L_D, are mostly irreversible and consistent with the results of sub-bandgap absorption spectra, where the density of occupied defect states decrease in the exposed state. Such decrease in the density of defect states could be a result of, for example, oxygen diffusion through and passivation of defects available on the surface of crystalline grains and column boundaries. In microcrystalline silicon films with I_C^{RS} < 0.30, increased amorphous phase caused better termination of crystalline column surfaces and less surface area is available for oxygen to passivate defects. For this reason no significant metastable changes were observed in microcrystalline silicon films with low crystallinity as well as in pure amorphous silicon films.

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