Plasma-enhanced chemical vapor deposition of intrinsic microcrystalline silicon from chlorine-containing source gas

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Abstract

Microcrystalline silicon (μc-Si:H) of truly intrinsic character can be deposited by plasma-enhanced chemical vapor deposition (PECVD) when dichlorosilane (SiH_2Cl_2) is added to the SiH_4-H_2 source gas. A dark-conductivity of $5\cdot10^{-8}$ S/cm, activation energy of 0.62 eV and photo-conductivity of $1\cdot10^{-5}$ S/cm are obtained. The optical bandgap for this material is approximately 1.1 eV. No special gas purification or microdoping is required. SiH_2Cl_2 added in small amounts has the additional effects of enhancing the crystallinity, and of reducing the oxygen incorporation by over a factor of two. Sub-bandgap absorption spectroscopy indicates a low defect density. VHF deposition yields material with lower defect density and higher photo-conductivity than material deposited using DC plasma excitation. Transition from amorphous to microcrystalline growth occurs during the first 100-150 nm of film growth. The oxygen content increases as the crystallinity increases. A first p-i-n solar cell with a 1.8 μm thick μc-Si:H(:Cl) i-layer exhibits V_{oc} = 0.35 V, I_{sc} = 4.14 mA/cm^2 and FF = 55 %, demonstrating device-quality material.

Introduction

Microcrystalline silicon (µc-Si:H) is a form of thin-film silicon which is of growing interest for device applications. P-i-n solar cells incorporating µc-Si:H as the absorbing layer produce high photo-current and are stable against light-soaking[1-3]. Thin-film transistors (TFTs) with µc-Si:H channel layers have higher on-currents than amorphous silicon TFTs[4-6].

µc-Si:H is deposited at substrate temperatures of 200-300ºC from highly H_2 diluted silane (SiH_4) by PECVD. Because of oxygen contamination[7,8] µc-Si:H is strongly n-type when deposited without special precautions. These donors reduce the electric field in part of the i-layer in a solar cell and thereby reduce the photocurrent collection efficiency. In a TFT, the unwanted oxygen doping causes undesirably high off-currents.

The oxygen donors can be compensated with boron at the ppm level ("microdoping"[1,9,10]). The need to tailor the boron doping to the case-by-case oxygen contamination and to control the doping within a very narrow window renders this method unsuitable for industrial practice. Truly intrinsic µc-Si:H has been obtained recently by purifying the gas with an oxygen getter and by carefully controlling the reactor condition[8]. A more robust deposition process which does not require additional equipment would be desirable for the production of µc-Si:H on an industrial scale.

In the present paper, we present a method for obtaining device-grade µc-Si:H by PECVD from SiH_4 and SiH_2Cl_2 diluted in H_2. Intrinsic material is deposited without any further measure and the growth process is very tolerant to changes in reactor conditions. Microcrystalline silicon using SiH_2Cl_2 as a precursor gas has been deposited at several laboratories[11-13], however without focussing on intrinsic material suitable for device-applications.

Experiment

All samples were deposited from SiH_4, SiH_2Cl_2 and H_2 at a substrate temperature of 210ºC, unless otherwise stated. The depositions were performed in a conventional three-chamber system with load-lock using DC plasma excitation. One sample and the solar cell were prepared using very high frequency (VHF) plasma excitation at 70 MHz at otherwise identical deposition conditions. The hydrogen dilution ratio $H_2/(SiH_4+SiH_2Cl_2)$ was kept constant at a value of ~35. Pressure during deposition was 0.9 torr. No special precautions were taken concerning the state of the reactor, such as pre-baking to reduce out-gassing from the walls. After ~30 min. heating in the load-lock, the substrates were transferred to the deposition chamber, followed by deposition. The base pressure before deposition was $\sim 1 \cdot 10^{-6}$ torr.

σ_d and σ_{ph} were measured under vacuum using thermally evaporated Al contacts of 7.5 mm length and 0.5 mm spacing. The temperature-dependence of σ_d was used to determine E_{act}. Photo-conductivity was measured using homogeneously absorbed light of $\lambda = 650$ nm wavelength and varying intensity; σ_{ph} values given in the text were obtained by extrapolation to a generation rate of 10^{21} $cm^{-3}s^{-1}$. A pronounced peak in the ultraviolet reflection spectrum at ~275 nm is a reliable indication for microcrystalline material[14,15]. We therefore measured reflection spectra between 200 and 400 nm and determined the height of the 275 nm peak as an indication of the crystallinity of the material. The optical absorption coefficient in the high-energy region was determined using UV/visible transmission spectra and following the procedure proposed by Swanepoel[16]. Sub-bandgap absorption spectra were measured using the constant photo-current method (CPM) on samples with the same contact geometry as for the conductivity measurements. The I-V curve of the solar cell was measured at ~25ºC using light of 100 mW/cm^2 intensity and a spectrum close to AM 1.5.

Results

μc-Si:H deposited with SiH_2Cl_2

Varying the $SiH_2Cl_2/(SiH_2Cl_2+SiH_4)$ ratio in the plasma between zero (pure H_2-diluted SiH_4) and one (pure H_2-diluted SiH_2Cl_2) resulted in the dark-conductivity σ_d, dark-conductivity activation energy E_{act} and photo-conductivity σ_{ph} values of Figure 1, for ~500 nm thick films. The μc-Si:H sample deposited from pure H_2 diluted SiH_4 exhibits a high σ_d in excess of 10^{-3} S/cm. E_{act} is <0.2 eV, reflecting high-level oxygen doping. Adding only a few percent of SiH_2Cl_2 reduces σ_d by over five orders of magnitude to $1.6\cdot10^{-8}$ S/cm, which is as low as the value obtained for μc-Si:H made by the microdoping or purifying techniques[8,9]. E_{act} is 0.62 eV. σ_d and E_{act} turn out to be very insensitive to the $SiH_2Cl_2/(SiH_2Cl_2+SiH_4)$ ratio R in the gas phase over the wide range of mixtures R from 0.08 to 0.33. For ratios $R \geq 0.5$, the films grow amorphous (Figure 2) and exhibit σ_d values of $<10^{-12}$ S/cm and E_{act} of ~1 eV. σ_{ph} of the μc-Si:H film deposited at $R = 0.08$ is $2\cdot10^{-6}$ S/cm; for films deposited with higher amounts of SiH_2Cl_2, σ_{ph} decreases gradually to $5\cdot10^{-7}$ S/cm at $R = 0.33$. SiH_2Cl_2 has the same effect on σ_d and E_{act} when using the VHF deposition technique, which has been found to be especially favorable to the deposition of μc-Si:H[17]. Values for the VHF-deposited sample at $R = 0.08$ are $\sigma_d = 5.4\cdot10^{-8}$ S/cm, $E_{act} = 0.62$ eV and $\sigma_{ph} = 1.0\cdot10^{-5}$ S/cm, the latter being almost an order of magnitude higher than for the best DC-deposited sample.

The growth rate is influenced only slightly by the $SiH_2Cl_2/(SiH_2Cl_2+SiH_4)$ ratio and is ~1 Å/s for all samples shown in Figure 1 and Figure 2, which were grown at the power density of ~100 mW/cm^2. Growth rates of 1.8 Å/s have been obtained by increasing the power density to

~280 mW/cm^2. The growth rate for the VHF sample at a power density of ~45 mW/cm^2 was 0.8 Å/s.

Figure 2 shows the height of the UV reflectance peak at 275 nm, normalized to the peak height for crystalline silicon, as a function of the SiH_2Cl_2 fraction. A small amount of SiH_2Cl_2 in the plasma is seen to enhance the crystallinity of the film. Upon further increase in SiH_2Cl_2, the crystallinity decreases and eventually the material becomes amorphous at $R \geq 0.5$. Raising the temperature enhances the crystallinity (Figure 2), while σ_d and E_{act} remain at their intrinsic values of ~10^{-8} S/cm and >0.6 eV, respectively. The crystallinity of the VHF-deposited sample is much higher than that of the equivalent DC sample, which explains the slightly higher σ_d at the same E_{act} compared to the DC-deposited sample.

Figure 3 shows optical absorption spectra obtained from UV/visible transmission and constant photocurrent method (CPM) spectroscopy. All samples were made at R = 0.08. Figure 3 features two ~500 nm thick films which are deposited using DC excitation at 210ºC and 280ºC and a ~750 nm thick VHF-deposited sample (210°C). The absorption spectrum of crystalline silicon is shown for comparison. The sample deposited at the higher temperature has a higher absorption coefficient for red wavelengths. The absorption coefficient in the low-energy region (~0.8 eV) of the CPM spectrum is an indication of the defect density[18-20]. The absorption coefficient at $h\nu = 0.8$ eV of the VHF-deposited sample is an order of magnitude lower than that of the DC-deposited sample. This indicates a lower defect density and correlates with σ_{ph}, which is an order of magnitude higher for the VHF-deposited than for the DC-deposited sample. The CPM spectrum of the VHF-deposited sample is comparable to device-grade µc-Si:H deposited without SiH_2Cl_2[20].

Determining the optical bandgap as the intersection of the $\sqrt{\alpha(h\upsilon)}$ plot with the energy axis[20], we obtain a value of roughly 1.1 eV for our μc-Si:H(:Cl) which is the same as the value for μc-Si:H deposited without SiH_2Cl_2[20]. An activation energy of ~0.6 eV means that the Fermi level lies close to midgap.

Figure 4 shows a cross-sectional SEM micrograph of the μc-Si:H(:Cl) film deposited at R = 0.08 and using VHF plasma excitation.

Effect of chlorine on oxygen incorporation

The presence of chlorine in the plasma reduces the oxygen content of μc-Si:H. Figure 5 shows SIMS depth profiles[21] for a sample consisting of three layers of μc-Si:H deposited with three different additions of SiH_2Cl_2. The top and bottom layers are a-Si:H encapsulating layers. Layer A was deposited using only SiH_4 and H_2. The oxygen content c_O of this layer is as high as $8{\cdot}10^{19}$ cm^{-3}, which explains its high σ_d of $4.1{\cdot}10^{-3}$ S/cm (Figure 1). Layer B was deposited with R = 0.08 at the same H_2 dilution ratio. In this layer, c_O is reduced by a factor of two to ~$4{\cdot}10^{19}$ cm^{-3}. The chlorine content c_{Cl} is 3-$4{\cdot}10^{19}$ cm^{-3}, which is nearly as high as c_O. For R = 0.17 (layer C), c_O decreases further to $3{\cdot}10^{19}$ cm^{-3} and c_{Cl} increases to 6-$7{\cdot}10^{19}$ cm^{-3}. Chlorine in the plasma therefore reduces c_O of the growing film whereas the growth rate is nearly unchanged. It is not clear whether the reduction of c_O can account for the intrinsic character of the films deposited with SiH_2Cl_2 or if other mechanisms take place, because c_O drops by a factor of two upon addition of SiH_2Cl_2 whereas σ_d drops by over 5 orders of magnitude.

Figure 6 shows c_O and c_{Cl} in our μc-Si:H for a larger set of samples. The addition of a small amount (R = 0.08) of SiH_2Cl_2 to the plasma reduces c_O by over a factor of two. Further additions of SiH_2Cl_2 has a smaller effect on c_O. c_{Cl} increases with increasing amount of SiH_2Cl_2 in the

plasma. Likewise, we show in Figure 1 that σ_d and E_{act} of the μc-Si:H samples made with the smallest addition of SiH_2Cl_2 (R = 0.08) already correspond to those of intrinsic films.

Possible explanations for the intrinsic character of μc-Si:H(:Cl) are a) a threshold value of c_O below which the doping effect of O is negligible, b) the p-type doping effect of Cl compensates the n-type doping of the O, or c) Cl deactivates O as a dopant. Let us briefly discuss these alternatives.

a) O acting as a dopant only above a certain concentration does not seem to be a probable explanation. However, one could imagine that a certain amount of O can be incorporated into the material without creating free carriers and therefore without shifting the Fermi level.

b) Cl has indeed been found to be a slight p-type dopant in a-Si:H[22,23]. However, whereas c_{Cl} and c_O are on the same order of magnitude for films deposited with small amounts of SiH_2Cl_2, c_{Cl} continues to increase with higher SiH_2Cl_2 ratios while c_O remains almost constant (Figure 6). σ_d would be expected to increase and E_{act} to decrease with increasing c_{Cl} if Cl were an efficient dopant.

c) One can imagine that Cl in the material could deactivate the doping effect of oxygen. The number of donors due to the presence of O could indeed be reduced if Si-O- or Si-O-H bonds in “regular” μc-Si:H were replaced by much stronger Si-O-Cl bonds in μc-Si:H(:Cl). At this point it can, however, not be excluded that another reason accounts for the fact that the energetic distribution of defects in μc-Si:H:Cl differs from that in “regular” μc-Si:H. The energetic position and charge state of the defect states will determine the position of the Fermi level.

Microcrystalline film growth and oxygen incorporation

σ_d is plotted for a thickness series of μc-Si:H deposited with R = 0.08 in Figure 7. For very thin films, σ_d corresponds to that of amorphous material. Note that σ_d of a-Si:H deposited with

SiH_2Cl_2 is usually 1-2 orders of magnitude lower than that of a-Si:H deposited from pure SiH_4[24]. Very thin samples are amorphous as the lack of a pronounced UV reflection peak confirms. σ_d and UV reflectance increase within the first 150-200 nm to the final value for bulk µc-Si:H films. Within approximately the same thickness range, i.e. 100-150 nm, the SIMS hydrogen depth profile shows the transition from a-Si:H to µc-Si:H with a lower H content (Figure 7, bottom). Interestingly, c_O also increases only gradually with increasing crystallinity, even though the gas mixture does not change and therefore the amount of O coming with the feedstock gases or from the chamber walls does not change either. We conclude therefore that the altered material structure of µc-Si:H compared to a-Si:H is the reason for the enhanced O incorporation. The time scale of the increase in the c_O (~25 min for 150 nm at 1 Å/s) excludes as an explanation O entrained with the feedstock gases and accumulating gradually in the chamber during deposition.

Solar cell

We tested our µc-Si:H(:Cl) in a solar cell with p-i-n structure (Figure 8). The i-layer thickness is 1.8 µm, the substrate is textured SnO_2 and the back contact is Ag which was thermally evaporated onto the n-layer, without a ZnO reflector layer in between. The solar cell shows a V_{oc} of ~350 mV and red response up to $\lambda = 1000$ nm (Figure 9). The fill factor is 55 %. Even though the short circuit current density value of 4.14 mA/cm^2 is low, the flat reverse-bias response suggests that the photo-carrier collection in forward bias is efficient. We believe that non-optimal optical performance (TCO haze, TCO reduction during deposition, lack of back reflector) cause the low photocurrent.

Conclusions

In conclusion, intrinsic μc-Si:H can be deposited in a PECVD process when chlorine is present in the plasma. A dark-conductivity of $5.4 \cdot 10^{-8}$ S/cm, activation energy of 0.62 eV and photo-conductivity of $1.0 \cdot 10^{-5}$ S/cm are obtained. The optical bandgap for this new material is approximately 1.1 eV. The deposition process does not require any gas purifying or microdoping procedures and is very insensitive to reactor conditions. A small amount of chlorine in the gas enhances the crystallinity of the material and reduces the amount of oxygen incorporated into the sample by over a factor of two. Sub-bandgap absorption spectroscopy indicates a low defect density in our material. VHF deposition yields material with lower defect density and higher photo-conductivity than material deposited using DC plasma excitation. Transition from amorphous to microcrystalline growth happens during the first 100-150 nm of film growth. The altered material structure of μc-Si:H compared to a-Si:H is the reason for the enhanced O incorporation as the oxygen content increases with increasing crystallinity during growth. A solar cell with a 1.8 μm thick μc-Si:H(:Cl) i-layer exhibits $V_{oc} = 0.35$ V, $I_{sc} = 4.14$ mA/cm^2 and FF = 55 %, proving that the material is suitable for device fabrication.

Acknowledgements

R. Platz thanks the Arthur u. Aenne Feindt Stiftung, Hamburg (Germany), and the Fondation Charles-Edouard Guillaume, Bienne (Switzerland) for funding of his stay at Princeton University. The Electric Power Research Institute supported this research.

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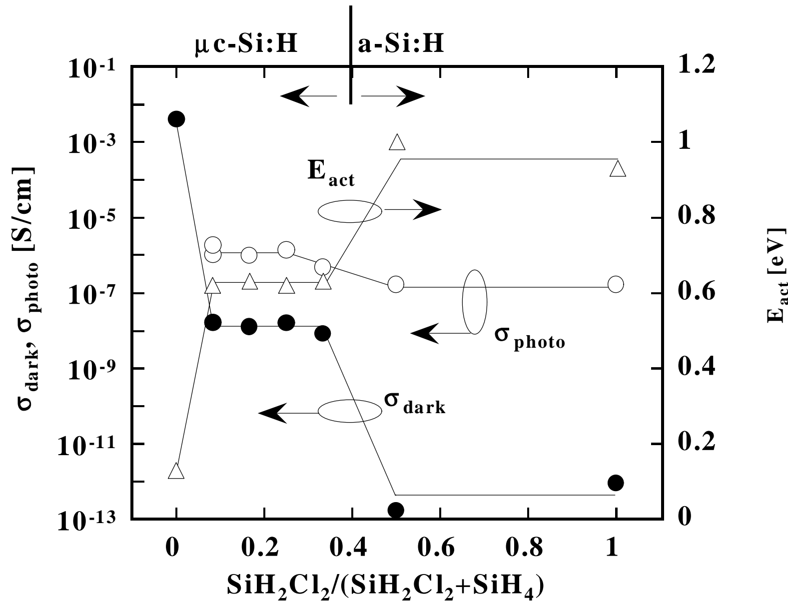
Figures



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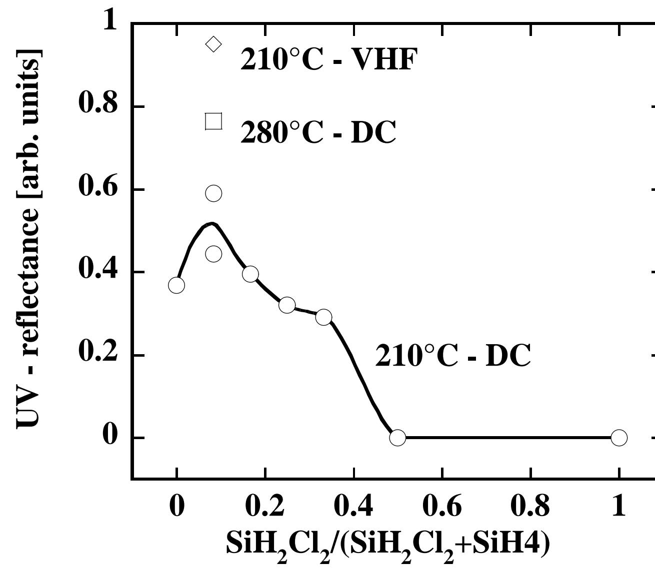

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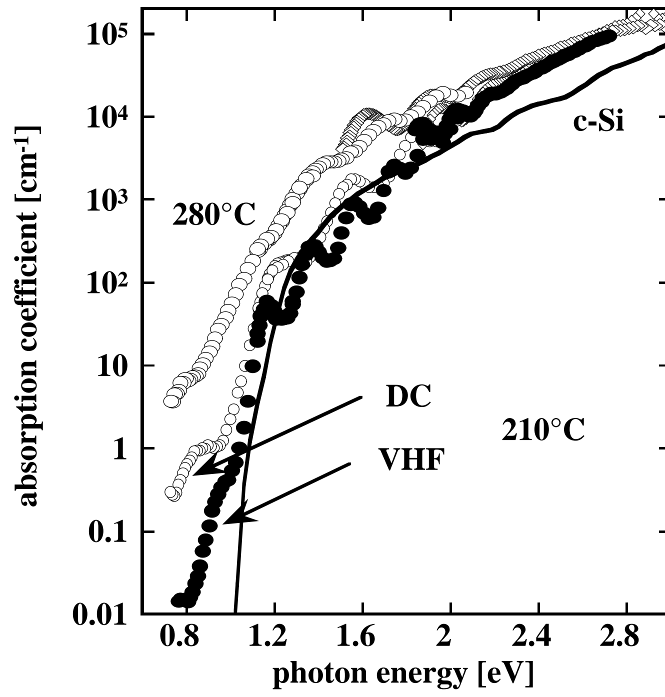

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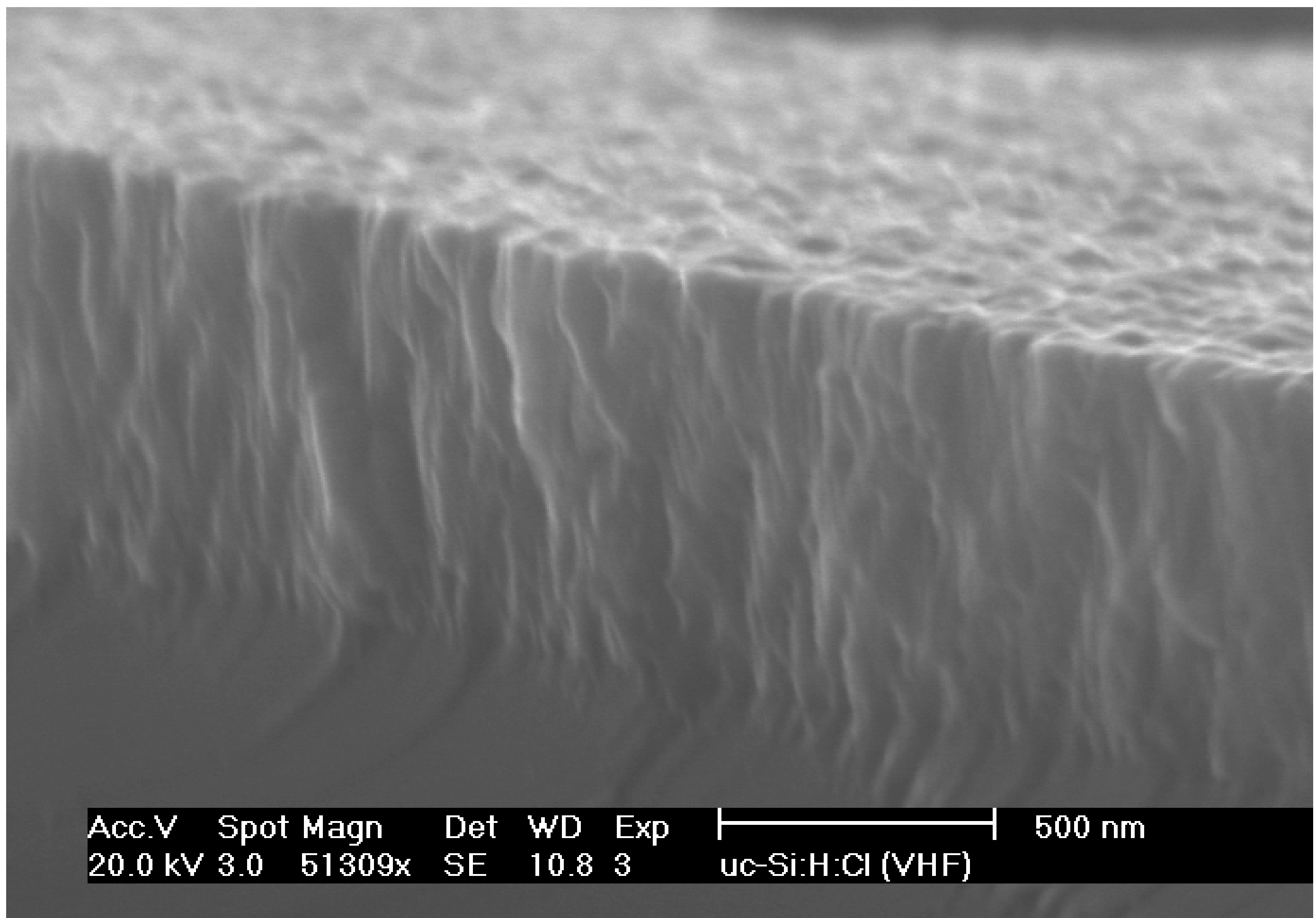

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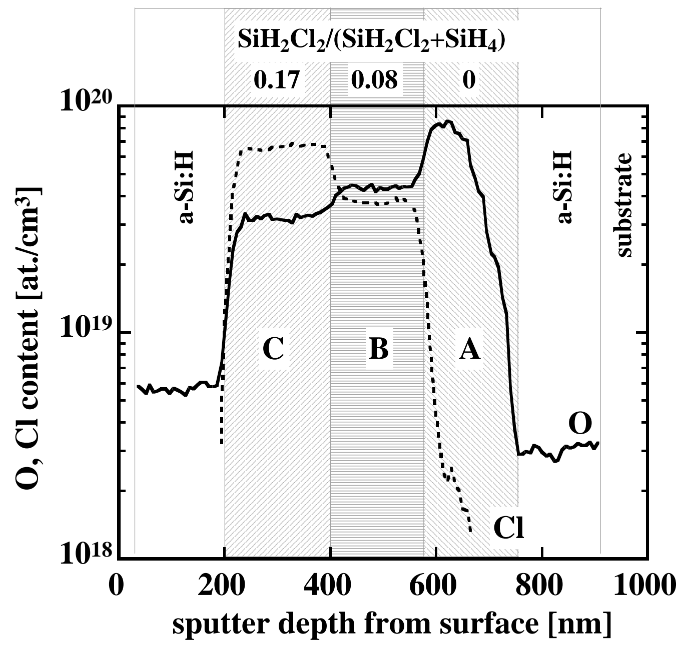

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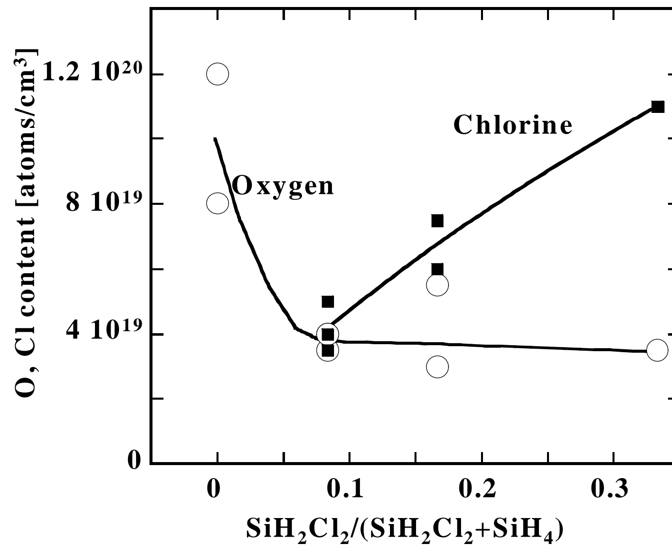

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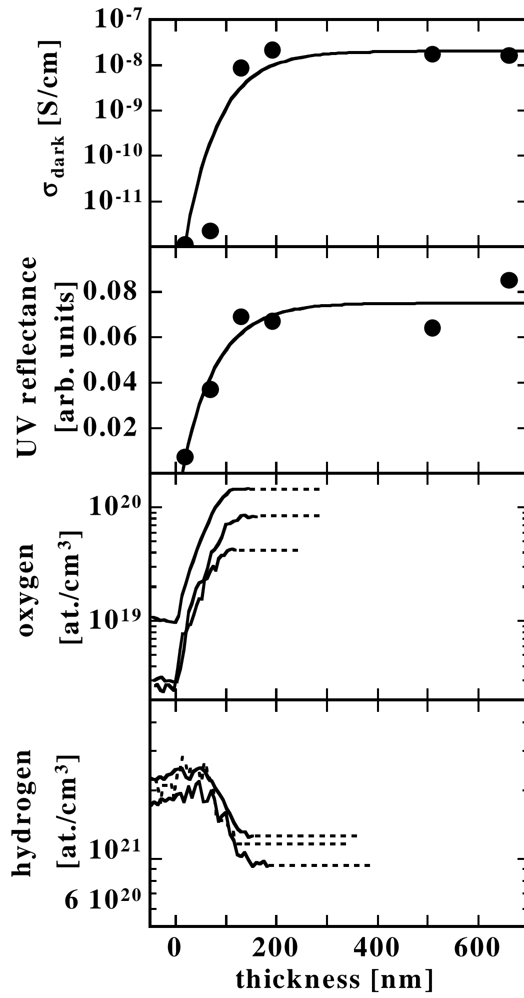

Figure 7

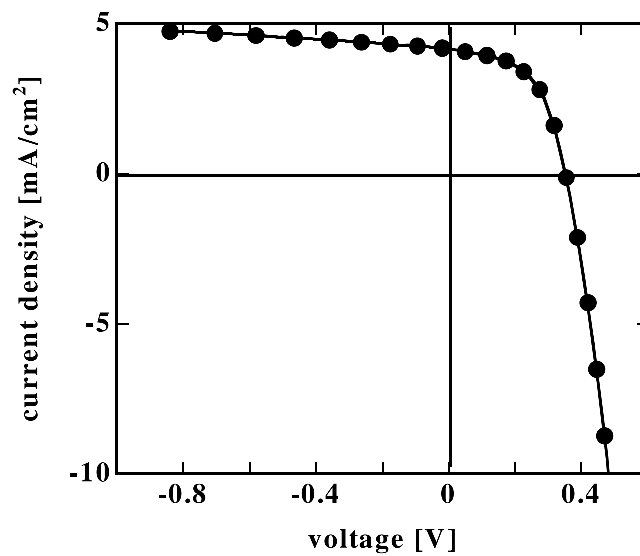

Figure 8

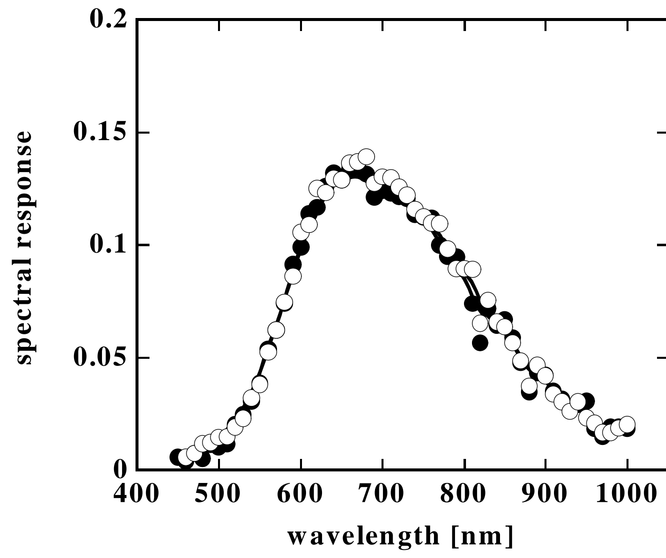

Figure 9

Figure captions

Figure 1: Dark-conductivity, dark-conductivity activation energy and photo-conductivity as functions of the amount of SiH_2Cl_2 in the gas phase for DC-deposited samples.

Figure 2: Ultraviolet reflectance at $\lambda = 275$ nm normalized to crystalline silicon.

Figure 3: Optical absorption spectra measured by constant photocurrent method (CPM) and UV/visible transmission spectroscopy for two substrate temperatures. Crystalline silicon is shown for comparison.

Figure 4: Cross-sectional SEM micrograph of a VHF-deposited µc-Si:H(:Cl) film on crystalline silicon substrate. SiH_2Cl_2 fraction is R = 0.08.

Figure 5: Oxygen and chlorine SIMS depth profile for µc-Si:H deposited on a-Si:H and capped with a-Si:H. The µc-Si:H layers were deposited with $SiH_2Cl_2/(SiH_2Cl_2+SiH_4)$ ratios of 0 (layer A), 0.08 (B), and 0.17 (C). Note the opposite trends in Cl and O concentrations. All layers are deposited using DC plasma excitation.

Figure 6: Oxygen and chlorine content in our µc-Si:H as a function of the SiH_2Cl_2 ratio. All layers are deposited using DC plasma excitation.

Figure 7: Top: dark-conductivity and UV reflectance for a thickness series of µc-Si:H deposited with a SiH_2Cl_2 / $(SiH_2Cl_2+SiH_4)$ ratio of 0.08 in a DC-excited plasma. Bottom: oxygen and hydrogen depth profiles from SIMS for µc-Si:H samples deposited with and without SiH_2Cl_2 in the plasma. The figure shows the transition from amorphous to microcrystalline silicon within the first 150 nm of growth. This transition and the increase in the oxygen content occur simultaneously.

Figure 8: I-V curve of a p-i-n solar cell with an i-layer of 1.8 µm thick µc-Si:H(:Cl) deposited by VHF.

Figure 9: Spectral response of the solar cell of Figure 8 measured at 0 V (I_{sc} conditions, black symbols) and -2 V (open symbols) bias.