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Intrinsic microcrystalline silicon by plasma-enhanced chemical vapor deposition from dichlorosilane

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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. A dark conductivity of 1.6×10^{-8} S/cm and an activation energy of 0.62 eV are obtained. No special gas purification or microdoping is required. SiH_2Cl_2 in small amounts has the additional effect of enhancing the crystallinity and reducing the oxygen incorporation by over a factor of 2. Sub-band-gap absorption spectroscopy indicates a low defect density.

Microcrystalline silicon (μc-Si:H) is of growing interest for device applications. *p-i-n* solar cells incorporating μc-Si:H as the absorbing layer produce high photocurrent and are stable against light soaking.[1,2] Thin-film transistors (TFTs) with μc-Si:H channel layers have higher on-currents than amorphous silicon TFTs.[3,4]

μc-Si:H is deposited at substrate temperatures of 200–300 °C from strongly H_2 diluted SiH_4 by plasma-enhanced chemical vapor deposition (PECVD). Because of oxygen contamination[5,6] 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’’[1,7,8]). The need to tailor the boron doping to the case-by-case content of oxygen and to control the doping within a very narrow window render this method unsuitable for industrial production. Truly intrinsic μc-Si:H has been obtained recently by purifying the gas with an oxygen getter and by carefully controlling the reactor condition.[6] 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.

We have discovered that μc-Si:H of intrinsic character can be deposited by PECVD from silane (SiH_4) and SiH_2Cl_2 diluted in H_2. Intrinsic material is obtained without any further measure and the deposition process is very tolerant to changes in reactor conditions.

All samples were deposited from SiH_4, SiH_2Cl_2, and H_2 at a substrate temperature of 210 °C, unless otherwise stated. The depositions were performed in a conventional multi-chamber system with load-lock. 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 prebaking to reduce outgassing 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 $\sim1\times10^{-6}$ Torr.

Varying the $SiH_2Cl_2/(SiH_2Cl_2+SiH_4)$ ratio in the plasma between zero (pure H_2-diluted SiH_4) and 100% (pure H_2-diluted SiH_2Cl_2) resulted in the dark-conductivity σ_d, dark-conductivity activation energy E_{act}, and photoconductivity σ_{ph} values of Fig. 1 for ~500 nm thick films.

The μc-Si:H sample deposited from pure H_2-diluted SiH_4 exhibits a high σ_d of $>10^{-3}$ S/cm. E_{act} is <0.2 eV indicating doping by oxygen at high level. Adding only a few percent of SiH_2Cl_2 produces a drop of σ_d by over five orders of magnitude to 1.6×10^{-8} S/cm, which is as low as the value obtained for μc-Si:H made by the microdoping or purifying technique.[6,7] 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 $\geqslant0.5$, the films grow amorphous (Fig. 2) and exhibit σ_d values of $<10^{-12}$ S/cm and E_{act} of ~1 eV. The σ_{ph} of the μc-Si:H film deposited at $R=0.08$ is 2×10^{-6} S/cm; for films deposited with higher amounts of SiH_2Cl_2,

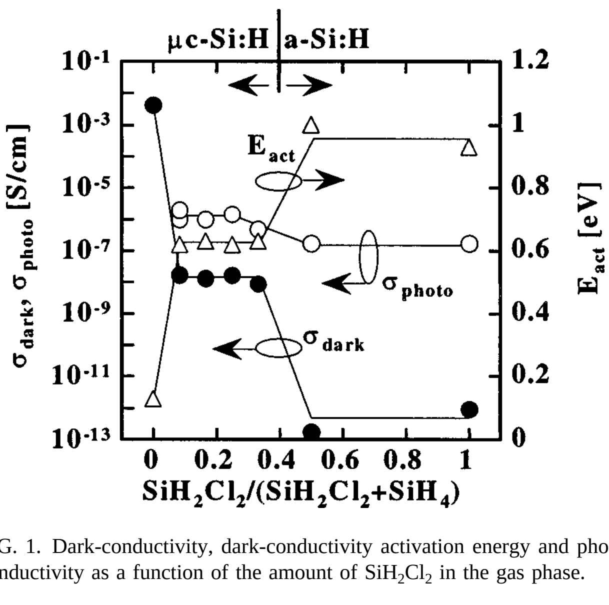

FIG. 1. Dark-conductivity, dark-conductivity activation energy and photoconductivity as a function of the amount of SiH_2Cl_2 in the gas phase.

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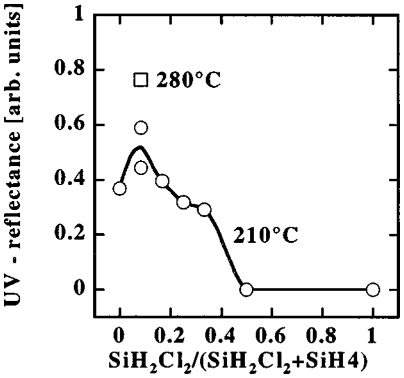

FIG. 2. Ultraviolet reflectance at λ = 275 nm normalized to crystalline silicon.

σ_{ph} decreases gradually to 5×10^{-7} S/cm at $R=0.33$.

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 Figs. 1 and 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.

A pronounced peak in the ultraviolet reflection spectrum at ~275 nm is a reliable indication for microcrystalline material.[9,10] Figure 2 shows the height of this UV reflectance peak, 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 enhances the crystallinity of the film. Upon further increase of SiH_2Cl_2, the crystallinity decreases and eventually the material becomes amorphous. Raising the temperature enhances the crystallinity (Fig. 2), while σ_d and E_{act} remain at their intrinsic values of $\sim10^{-8}$ S/cm and >0.6 eV, respectively.

Figure 3 shows the optical absorption spectrum obtained from UV/visible transmission and constant photocurrent method (CPM) spectroscopy for two 500 nm thick films deposited with $R=0.08$ at 210 and 280 °C, and that of crystalline silicon. The sample deposited at the higher temperature absorbs more strongly in the red, indicating a higher crystalline fraction, which confirms the UV reflectance data of Fig. 2. The absorption coefficient in the low-energy region (~0.8 eV) of the CPM spectrum is an indication of the defect density.[11–13] The defect density in our material is low, because the CPM spectrum is comparable to device-grade μc-Si:H deposited without SiH_2Cl_2.[13]

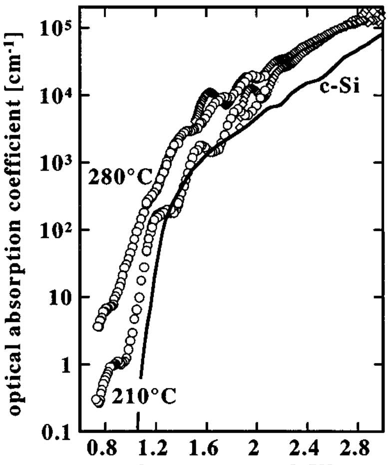

FIG. 3. Optical absorption spectra as measured by constant photocurrent method (CPM) and transmission for two substrate temperatures. Crystalline silicon is shown for comparison.

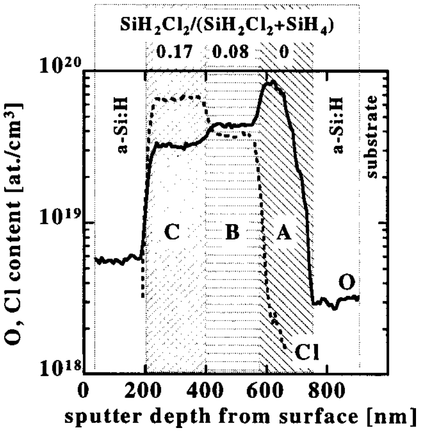

FIG. 4. Oxygen and chlorine SIMS depth profile for μc-Si:H deposited on a-Si:H and capped with a-Si:H. The μc-Si:H layers were deposited with $SiH_2Cl_2/(SiH_2Cl_2+SiH_4)$ ratios of 0 (layer A), 0.08 (B), and 0.17 (C). Note the opposite trends in Cl and O concentrations.

Addition of SiH_2Cl_2 reduces the oxygen content of μc-Si:H. Figure 4 shows secondary ion mass spectroscopy (SIMS) depth profiles[14] for a sample consisting of three layers of μc-Si:H deposited with varying amounts 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 8×10^{19} cm^{-3}, which explains the high value of its σ_d of 4.1×10^{-3} S/cm (Fig. 1). Layer B was deposited at $R=0.08$ at the same H_2 dilution ratio. In this layer, c_o is reduced by a factor of two to $\sim4\times10^{19}$ cm^{-3}. The chlorine content c_{Cl} is $2-3\times10^{19}$ cm^{-3}, which is nearly as high as c_o. For $R=0.17$ (layer C), c_o decreases further to 3×10^{19} cm^{-3} and c_{Cl} increases to $6-7\times10^{19}$ cm^{-3}. Adding chlorine to 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 2 upon addition of SiH_2Cl_2 whereas σ_d drops by over five orders of magnitude.

Incorporating μc-Si:H:Cl in solar cells (Fig. 5) produces V_{oc} values of over 450 mV and red response up to $\lambda = 1000$ nm. Current collection, however, is strongly voltage dependent, resulting in a low FF of 37%. We do not yet

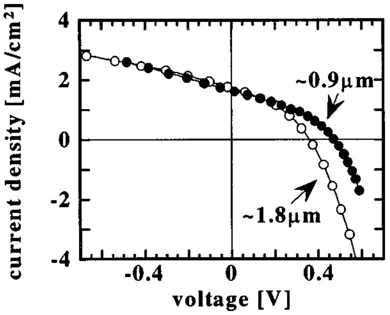

FIG. 5. $I-V$ curve of solar cells with μc-Si:H:Cl i layers (0.9 and 1.8 μm).

know if the current collection will improve with process optimization, or if it is inherent to the *i*-layer material.

In conclusion, intrinsic μc-Si:H can be deposited in a PECVD process when chlorine is present in the plasma. Dark-conductivity and activation energy values for this material are 1.6×10^{-8} S/cm and 0.62 eV, respectively. 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 2. Sub-band-gap absorption spectroscopy indicates a low defect density in this new material. First solar cells show good V_{oc} values but so far unsatisfactory current collection.

Note added in proof: The most recent solar cell has a short-circuit current density of >6 mA/cm^2.

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