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Highly transparent microcrystalline silicon carbide grown with hot wire chemical vapor deposition as window layers in *n-i-p* microcrystalline silicon solar cells

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Microcrystalline silicon carbide ($\mu\text{c-SiC}$) films were prepared using hot wire chemical vapor deposition at low substrate temperature. The $\mu\text{c-SiC}$ films were employed as window layers in microcrystalline silicon ($\mu\text{c-Si:H}$) *n-i-p* solar cells. Quantum efficiency (QE) and short circuit current density (J_{SC}) in these *n*-side illuminated *n-i-p* cells were significantly higher than in standard *p-i-n* cells. A high QE current density of 26.7 mA/cm² was achieved in an absorber layer thickness of 2 μm . The enhanced J_{SC} was attributed to the wide band gap of the $\mu\text{c-SiC}$ layer and a sufficiently high hole drift mobility in $\mu\text{c-Si:H}$ absorber layer. © 2007 American Institute of Physics. [DOI: 10.1063/1.2739335]

With its wide optical band gap, silicon carbide (SiC) is a good candidate as a solar cell window layer material. For thin film silicon [amorphous silicon (*a-Si:H*) and microcrystalline silicon ($\mu\text{c-Si:H}$)] solar cells, using a cheap glass substrate, low process temperatures, e.g., 200 °C are essential. However, high-quality SiC films were usually obtained at high substrate temperatures, e.g., 700 °C.¹ Therefore, efforts were made for a low-temperature growth of $\mu\text{c-SiC}$ films.^{2–7} Recently, growth of $\mu\text{c-SiC}$ films at substrate temperatures lower than 400 °C was achieved by using hot wire chemical vapor deposition (HWCVD).^{5–7} Although no doping gases were used during the depositions, the $\mu\text{c-SiC}$ films were found to be highly conductive. Hall effect measurements revealed that the $\mu\text{c-SiC}$ films were *n* type.^{6,7} Apart from its low deposition temperature and high conductivity, the high transparency of such $\mu\text{c-SiC}$ films matches the requirements of $\mu\text{c-Si:H}$ or *a-Si:H* solar cell window layers very well. For the typical film thickness of 20 nm, the absorption loss is less than 3% (0.3%) in the spectral region where the absorption coefficient is less than 10⁴ (10³) cm^{−1}, respectively. In addition, its refractive index of about 2.5 is advantageous for reducing the cell reflectivity.

It has been well established that *a-Si:H* solar cells need an illumination through the *p*-type side in order to get optimum stabilized performance. This is partially caused by the fact that the hole drift mobility (HDM) in *a-Si:H* films is two to three orders of magnitudes lower than the electron mobility.⁸ Differently, the HDM in $\mu\text{c-Si:H}$ films is much higher than in *a-Si:H* films. Time-of-flight studies made on $\mu\text{c-Si:H}$ *p-i-n* diodes demonstrated that the electron and hole drift mobilities in $\mu\text{c-Si:H}$ films with crystalline volume fractions >0.35 were as high as 3.8 and 1.3 cm²/(V s), respectively.^{9,10} Nearly identical quantum efficiency (QE) curves were obtained for $\mu\text{c-Si:H}$ solar cells under *p*- and *n*-side illuminations, showing a symmetrical photocurrent collection.¹¹ The high HDM and the high transparency of the $\mu\text{c-SiC}$ layers offer a high potential for an application of the $\mu\text{c-SiC}$ window layers in *n-i-p* $\mu\text{c-Si:H}$ solar cells.

In this letter we report an application of such HWCVD grown, unintentionally doped $\mu\text{c-SiC}$ films as window layers in *n-i-p* $\mu\text{c-Si:H}$ solar cells.

The $\mu\text{c-SiC}$ films and $\mu\text{c-Si:H}$ solar cells were prepared in a “cluster-tool” system with three plasma enhanced chemical vapor deposition chambers and one HWCVD chamber.^{5,12} The gas mixture for the $\mu\text{c-SiC}$ films growth was 0.3% monomethylsilane diluted in hydrogen. For the solar cells the $\mu\text{c-SiC}$ films were deposited at a filament temperature (T_F) of 2000 °C and a substrate temperature (T_S) of 250 °C. The $\mu\text{c-SiC}$ films were characterized with Raman spectroscopy, Fourier transform infrared (FTIR) absorption spectroscopy, photothermal deflection spectroscopy (PDS), secondary ion mass spectrometry (SIMS), and dark electrical conductivity measurements.

n-i-p solar cells were prepared on textured glass/ZnO:Al substrates¹³ with a deposition sequence of $\mu\text{c-SiC}/\mu\text{c-Si:H}(i)/\mu\text{c-Si:H}(p)$. For means of comparison, *p-i-n* $\mu\text{c-Si:H}$ solar cells were also prepared using $\mu\text{c-Si:H}(p)$ window layers. The active area of each cell was 1 cm² as defined by the geometry of the Ag back contact. For a better light trapping, ZnO:Al/Ag back contacts were used in some cells. The *J-V* characteristics of the solar cells were measured under AM1.5 illumination at 25 °C. The *p-i-n* and *n-i-p* solar cells were illuminated through the *p* and *n* sides of the cells, respectively.

The presence of $\mu\text{c-SiC}$ (in contrast to $\mu\text{c-Si}$ embedded *a-Si_{1-x}C*) is proven by Raman spectroscopy which shows two strong vibration modes at about 796 and 965 cm^{−1}, ascribed to the transverse optical mode and the longitudinal optical mode of SiC,^{5–7} respectively. In addition, FTIR absorption measurements exhibit a sharp peak around 800 cm^{−1}, corresponding to a SiC stretching mode.⁵ Figure 1 shows a typical absorption spectrum of $\mu\text{c-SiC}$ films with a thickness around 150 nm deposited under the same condition as those used in solar cells, measured by PDS. For a comparison, typical absorption spectra of *n*-type *a-Si:H* and $\mu\text{c-Si:H}$ films are also plotted in Fig. 1. It can be seen that the optical absorption edge of the $\mu\text{c-SiC}$ film is shifted considerably towards higher photon energy with respect to those in *n*-type *a-Si:H* and $\mu\text{c-Si:H}$ films approaching an E_{04} (energy where the absorption coefficient α is 10⁴ cm^{−1})

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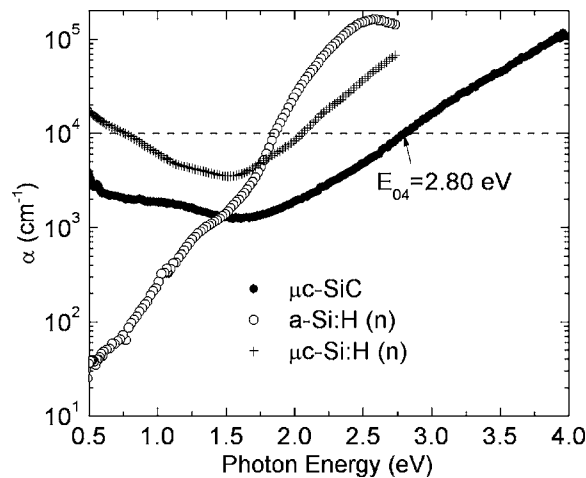


FIG. 1. Typical PDS curves of the $\mu\text{c-SiC}$ films used as window layers in $\mu\text{c-Si:H}$ solar cells as well as the n -type $a\text{-Si:H}$ and $\mu\text{c-Si:H}$ films.

of 2.8 eV. It is also shown in Fig. 1 that the subgap absorption of the $\mu\text{c-SiC}$ and $\mu\text{c-Si:H}$ films is high and increases towards lower energy. This indicates the predominant absorption by free carriers masking the absorption by defect states observed in films of lower doping level. Recent Hall effect measurements revealed the n -type nature of such $\mu\text{c-SiC}$ films.⁷ Nitrogen and oxygen are the dominant impurities under the present deposition condition. It is known that nitrogen is the most important shallow donor impurity used in SiC crystal growth.¹⁴ SIMS measurements reveal that the concentration of nitrogen ($[\text{N}] \sim 2.4 \times 10^{19} \text{ cm}^{-3}$) in the $\mu\text{c-SiC}$ films is higher than that of free carriers ($n \sim 1.7 \times 10^{19} \text{ cm}^{-3}$). However, $[\text{N}]$ decreases with increasing T_s , while n increases. At $T_s \geq 400^\circ\text{C}$, n becomes much higher than $[\text{N}]$. Therefore, even if nitrogen is a doping source in the $\mu\text{c-SiC}$ films, a second doping source exists, in particular, in films deposited at high T_s . It has been reported that oxygen can also contribute to the n -type doping in SiC by forming oxygen related shallow donors.^{15–18} One oxygen related shallow donor can either be a cluster defect containing many oxygen atoms^{15–17} or be an isolated oxygen impurity on the carbon site (O_C).¹⁸ According to the oxygen cluster model, n should be one to two orders of magnitude lower than $[\text{O}]$. However, the SIMS measurements indicate that in most cases the concentration of oxygen $[\text{O}]$ ranges is just about two to three times of n . With respect to the values of n and $[\text{O}]$, the present experimental result prefers the O_C model. Nevertheless, it is not clear now whether only the oxygen or both the nitrogen and oxygen contribute to the n -type doping. More effort is needed to identify the donors in the $\mu\text{c-SiC}$ films.

Figure 2 plots solar cell parameters of the p - i - n and n - i - p solar cells (i -layer thickness = $1 \mu\text{m}$) deduced from J - V characteristics, i.e., efficiency η , fill factor (FF), short circuit current density (J_{SC}), and open-circuit voltage (V_{OC}), as a function of silane concentration (SC) used for the deposition of i layers. SC is defined by the ratio of the process gas flows, i.e., $\text{SC} = [\text{SiH}_4]/([\text{SiH}_4] + [\text{H}_2])$. For both types of cells, η and FF increase upon increasing SC until a sudden decrease appears at a certain SC. It is believed that at this SC the columnar crystalline growth collapses and a considerable amorphous volume fraction appears in the i layer and reduces the absorption in at long wavelength.¹⁹ It is also found

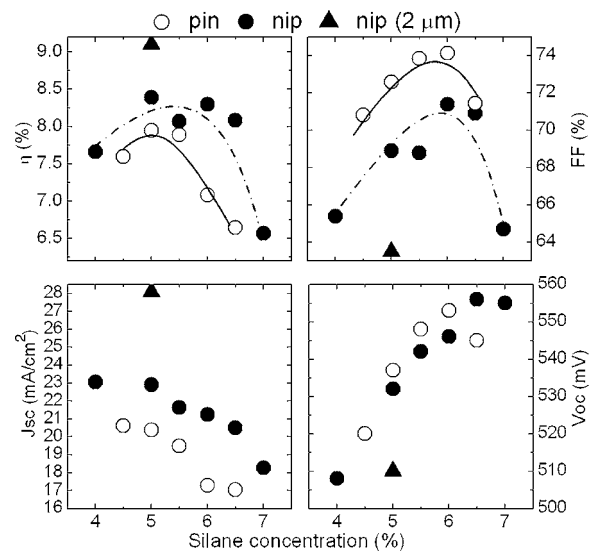


FIG. 2. J - V characteristics, η , FF, J_{SC} , and V_{OC} of $\mu\text{c-Si:H}$ solar cells plotted as a function of silane concentration (SC) used for the deposition of $\mu\text{c-Si:H}$ i layers. Without specific note, the absorber layer thickness of cells is $1 \mu\text{m}$. The J_{SC} of the $2\text{-}\mu\text{m}$ -thick nip cell was deduced by multiplying the QE current with a factor of 1.05. The lines are guide to the eyes.

that V_{OC} and J_{SC} evolve almost linearly in the investigated SC regime. The similarity in the J - V characteristics of the n - i - p and the p - i - n cells suggests that the cell performance mainly depends on i -layer properties. It can also be seen in Fig. 2 that the FF values for the n - i - p cells are lower than those for p - i - n cells. It is not clear whether the low FF values in the n - i - p cells compared to those in the p - i - n cells can be attributed to a stronger incorporation of defects during a growth of $\mu\text{c-Si:H}$ i layer on $\mu\text{c-SiC}$ layer instead of on a $\mu\text{c-Si:H}$ p layer. Despite of the lower FF values, the much higher short circuit current densities are obtained for the n - i - p cells, which lead to the higher η as compared to the p - i - n cells. Solar cells have also been measured under the illuminations of a modified AM1.5 spectrum with a red cut-on filter OG590 ($\lambda > 590 \text{ nm}$) or a blue band filter BG7 (with λ around 480 nm), corresponding to charge carrier generation profiles that are rather homogeneous over the i layer or rather close to the window layer, respectively. It is found that the FF values of the n - i - p cells illuminated under the blue and red filters are always lower than those for p - i - n cells. This observation indicates that the interface effect (between the n and i layers) is not the only effect deciding the low FF value in n - i - p cells shown in Fig. 2. It is seen in Fig.

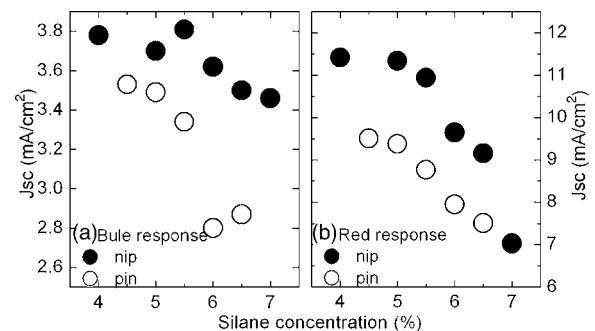


FIG. 3. Short current densities (J_{SC}) for $1\text{-}\mu\text{m}$ -thick p - i - n and n - i - p solar cells plotted as a function of SC. The J_{SC} values are determined from J - V measurements under an illumination of (a) AM1.5 spectrum+blue filter or (b) AM1.5 spectrum+red filter.

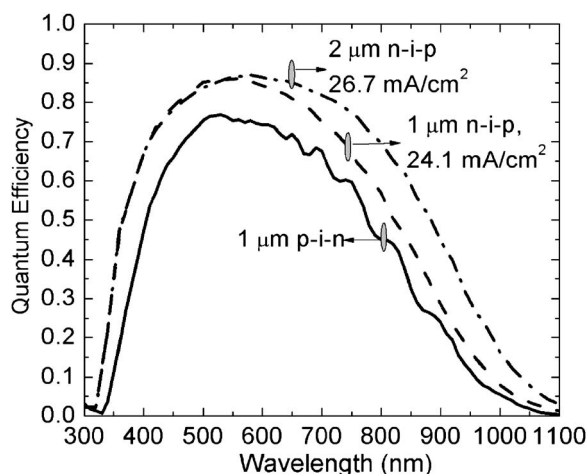


FIG. 4. Quantum efficiency (QE) curves of one *p-i-n* cell and two *n-i-p* cells. The QE curve for the *p-i-n* cell is taken from Ref. 10.

3 that the *n-i-p* cells show much higher J_{SC} values than the *p-i-n* ones under both kinds of illuminations. This result indicates that the enhanced light absorption for the *n-i-p* cells occurs in the whole spectral regimes. This observation is in accordance with the result of QE measurements. Figure 4 shows the QE curves of one *p-i-n* cell and two *n-i-p* cells. ZnO:Al back reflectors are used in these cells for a better light trapping. It is found that for the 1- μm -thick cells, the *n-i-p* diode shows much higher QE than the *p-i-n* structure in the entire spectral region.

The high QE and J_{SC} observed in the *n-i-p* cell can be attributed to two effects: (i) the higher transparency of the $\mu\text{c-SiC}$ films [compared to the $\mu\text{c-Si:H}(p)$ films] and (ii) a sufficiently HDM in the $\mu\text{c-Si:H}$ *i* layer. The first effect allows an enhanced light penetration through the window layer and consequently a higher generation of photocurrent in absorber layers of the *n-i-p* cells; the second one ensures a sufficient diffusion length of holes and in turn an efficient photocurrent collection. The enhanced short circuit current densities in these *n-side* illuminated *n-i-p* cells provide an experimental evidence for the symmetrical collection of carriers in $\mu\text{c-Si:H}$ films as proposed in previous works.^{9–11} In addition, the good performance of the *n-i-p* solar cells verifies that the *n-type* doping level in the $\mu\text{c-SiC}$ films is high enough to shift the Fermi level towards the conduction band edge to build up a sufficient electric field.

Furthermore, it is shown in Fig. 4 that an increase of *i* layer thickness from 1 to 2 μm leads to a considerable enhancement of the spectral response of the *n-i-p* cells in the spectral region with $\lambda > 560$ nm. With this strong spectral

response, a very high QE current density of 26.7 mA/cm^2 is achieved in an *i*-layer thickness of 2 μm , which leads to a solar cell efficiency of 9.1%.

In conclusion, unintentionally *n-type* doped $\mu\text{c-SiC}$ films grown with HWCVD at low substrate temperature have been used as the window layers in $\mu\text{c-Si:H}$ solar cells. Short circuit current densities are significantly improved due to the use of the $\mu\text{c-SiC}$ window layers with a wide optical band gap. The excellent cell performance shown by the *n-side* illuminated *n-i-p* cells confirms a significantly enhanced HDM in $\mu\text{c-Si:H}$ films as compared to that in *a-Si:H* films.

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