Hot Wire CVD : A One-step Process to Obtain Thin Film Polycrystalline Silicon at a Low Temperature on Cheap Substrates.

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ABSTRACT

Polycrystalline silicon films have been prepared by Hot Wire Chemical Vapor Deposition (HWCVD) at a relatively low substrate temperature of 430°C. The optimized material has 95% crystalline volume fraction with an average grain size of ~70 nm preferentially oriented along the (220) direction. The optical band gap calculated from optical absorption by photothermal deflection spectroscopy (PDS) showed a value of 1.1eV, equal to crystalline silicon. An activation energy of 0.54 eV for the electrical transport confirmed the intrinsic nature of the films. A low dangling bond defect density of $\sim 10^{17}/cm^3$, a high minority carrier diffusion length of 334 nm and a majority-carrier mobility-lifetime ($\mu\tau$) product of 7.1×10^{-7} cm^2V^{-1} ensure that the poly-Si films possess device quality. A single junction n-i-p cell made in the configuration n^+-c-Si/i-poly-Si:H/p-μc-Si:H/ITO/Ag yielded 3.15% efficiency under $100 mW/cm^2$ AM1.5 illumination.

1. Introduction

To make the fabrication of photovoltaic (PV) devices cost effective, a low temperature process on cheap foreign substrates at a high deposition rate is essential. P-i-n microcrystalline silicon cells using the very high frequency (VHF) plasma CVD process at a low temperature have yielded 7.7% stable efficiency [1]. However, the deposition rate is too low (<2Å/s) for commercial use. Hot-wire chemical vapor deposition (HWCVD) process satisfies all the requirements of a low-cost single-step fabrication of polycrystalline silicon thin films. Though many groups have claimed success in obtaining good quality poly-Si films by HWCVD, the successful demonstration of incorporation of these materials in a solar cell has not been presented so far. To that end, we have optimized deposition parameters to obtain device-quality poly-Si films and present here the first successful solar cell results by fabricating an n-i-p cell using poly-Si as the i-layer.

2. Experimental

Poly-Si films were deposited on 10 cm x10 cm Corning 7059 glass and on c-Si wafer substrates by HWCVD in one of the chambers of an ultra high vacuum multi-chamber system (PASTA). The p-μc-Si films were deposited by PECVD in a separate chamber of the same system. The thicknesses and deposition rates of the films were measured with a Dektak profilometer and reflection/transmission measurements.

Single-junction cells were fabricated on highly-doped n^+-c-Si wafer in the configuration n^+-c-Si/i-poly-Si:H/p-μc-Si:H/ITO/Ag. Cells were characterized by light and dark I-V and spectral response measurements.

3. Results and Discussion

To obtain polycrystalline Si films, the source gas SiH_4 was diluted with hydrogen while the other parameters were fixed. The crystallinity depends strongly on the hydrogen dilution ratio SiH_4/H_2 (r) values. The x-ray diffraction (XRD) spectra of polysilicon films show that at a higher r (>10%) the grains are preferentially oriented along the (220) direction. Fig. 1 shows the dependence of the crystalline volume fraction (V_f), estimated from the Raman spectrum [2], and the crystalline grain size (x), calculated from XRD by the Scherrer formula [3], on the SiH_4/H_2 ratio. It is observed that with increasing r, V_f increases upto a maximum of 94.6% at an r value of 10% and the grain size along the (220) direction increases with a simultaneous decrease along the (111) direction. AFM pictures reveal that at r=10% the feature dimentions, which may consist of multiple grains, are big (~0.5μm) and needle type with complete coalescence of grains. Figure 2 shows that at r=10% the activation energy (E_a) reaches a minimum value of 0.54 eV and the minority carrier diffusion length (L), determined by steady state photocarrier grating technique (SSPG) reaches a maximum value of 220 nm. This could be attributed to the increase in crystalline volume fraction that creates less grain boundary defects ($\sim 10^{17}$/cc at r=10%, deduced from electron spin resonance (ESR)). The μτ-product of the majority carrier, obtained under 700 nm monochromatic light with a flux of 10^{15} cm^{-2} s^{-1}, is $7.1 \times 10^{-7} cm^2V^{-1}$.

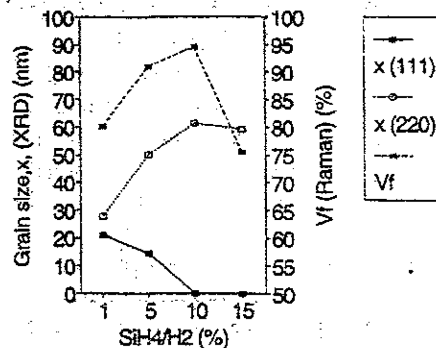

Fig.1 : Grain sizes (x) along (111) and (220) orientations and the crystalline volume fraction (V_f) at different SiH_4/H_2.

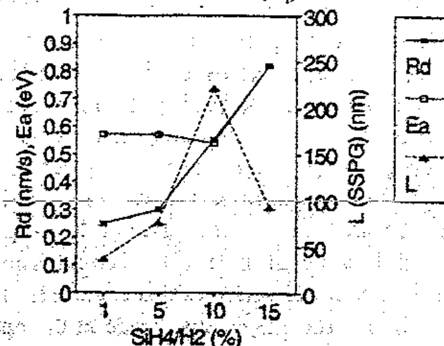

Fig.2 : Deposition rate (R_d), activation energy (E_a) and ambipolar diffusion length (L) at different SiH_4/H_2.

The band gap, estimated from $\sqrt{\alpha}$ vs E(eV) plot (Fig. 3) by photothermal deflection spectroscopy (PDS), shows a value of 1.1 eV for the sample obtained at r=10%, equal to crystalline silicon. The activation energy of 0.54 eV for the band gap of 1.1 eV implies that the Fermi level is at the center of the gap. This is achieved without boron compensation or use of a gas purifier. The fast deposition rate (5.5Å/s) and a better vacuum in the chamber ensures less oxygen incorporation into the network. Moreover the compactness of the structure prohibits in-diffusion of oxygen into the network. This was confirmed by the IR spectrum where no oxygen line at 1050 cm^{-1} (corresponding to SiO bonds) was observed even after several days of exposure to air and the diffusion length showed no decline in the same period.

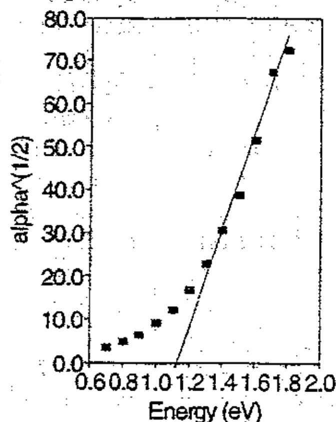

Fig.3 : Square root of the absorption coefficient (α) versus energy (E) measured by PDS.

As described above, in the dilution series at a wire temperature of 1900°C, the poly-Si film with the best quality is achieved at a SiH_4/H_2 ratio of 10 %. At this SiH_4/H_2 value, the wire temperature was varied to improve the material quality further. At a T_w of 1800°C, the diffusion length increased substantially to a high value of 334 nm. The photoconductivity (σ_{ph}) of 1.9×10^{-5} Ω^{-1} cm^{-1} has been achieved. The IR spectrum showed that the absorption at 2100 cm^{-1} is completely absent and the stretching vibration is concentrated at 2000 cm^{-1}, corresponding to Si-H mode only. The total hydrogen content measured from the wagging mode (640 cm^{-1}) is only 0.47 %. However, the crystalline volume fraction and the average grain size and orientation of grains remained similar to the poly-Si films made at T_w of 1900 °C.

Cell Properties

We fabricated n-i-p cells as a test structure for the intrinsic poly-Si layers in the configuration n^+-c-Si(Wafer)/i-poly-Si:H(HWCVD)/p-µc-Si:H(PECVD)/ITO/Ag. The hot-wire chamber is part of the multi-chamber system. The properties of the p-µc-Si:H layers have already been tested in other devices [4]. We have used heavily doped n^+-c-Si layers to serve as the substrate and as the n-layer of the n-i-p cell to ensure that this does not contribute to the current. The above method leaves us with fewer variables that could influence the solar cell as a whole. The i-layer was made at the optimum condition of T_w = 1800 °C, T_s=430 °C, P_r=0.1 mbar and SiH_4/H_2 ratio of 10%. There is a 3 nm wide band gap buffer layer before the p-layer, which helps to improve the cell properties. We achieved an efficiency of 3.15% for an unoptimized cell. The I-V characteristics are shown in Fig.4. A V_{oc} of 0.49 V was achieved. However, the fill factor (0.38) needs a lot of improvement. A reasonably high J_{sc} of ~20 mA/cm^2 could be achieved in most cells while the i-layer was only 1.5 µm thick. There may be some unintentional beneficial light scattering due to the native texture of the poly-Si layers. AFM picture reveals such a texture in the poly-Si films. [5]

4. Conclusions

Device-quality poly-Si films have been obtained by the HWCVD method. We have shown that it is possible to obtain poly-Si films with the Fermi level at the center of the gap even without boron micro-doping or the use of a gas purifier. Grains showed preferential orientations and the materials have ~95 % crystalline volume fraction with an average grain size of ~70 nm making a compact structure. The high minority carrier diffusion length of 334 nm makes these poly-Si films very promising for solar cell applications. We have demonstrated the device performance of n-i-p cells with poly-Si as active intrinsic layer. An efficiency of 3.15 % and a current of 20 mA/cm^2 have been achieved in an only 1.5 µm thick i-layer.

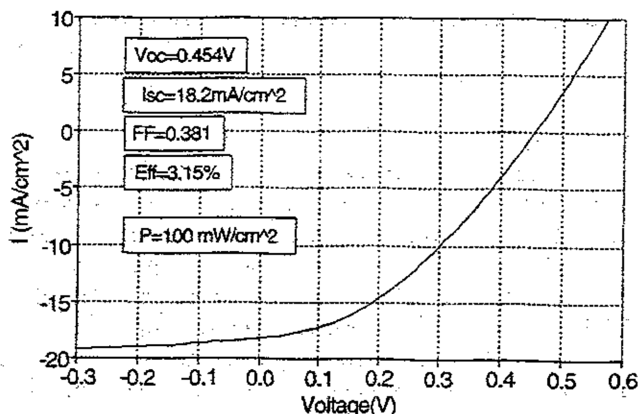

Fig.4 : I-V characteristics of an n-i-p cell with poly-Si i-layer of thickness ~1.5 µm.

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