Crystal growth characterization of polycrystalline silicon films obtained by hot-wire chemical vapour deposition

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ABSTRACT: Polycrystalline silicon (poly-Si) films were obtained at moderate temperatures (280-500°C) from a mixture of silane and hydrogen in a hot wire CVD reactor. SEM and TEM results revealed a columnar growth of poly-Si grains with a preferential orientation of the crystals perpendicular to the substrate surface along the [110] direction. Plan view examinations along the [110] axis revealed a needled shape of the crystals (0.3-1 μm) with the largest axis randomly distributed on the plane. The high quality of the polycrystalline samples obtained makes the hot-wire technique very promising.

1. INTRODUCTION

Polycrystalline silicon films have a great interest owing to their wide range of applications in large area optoelectronic and photovoltaic devices, such as thin film transistors for active displays and solar cells, respectively.

Several methods have been used to obtain poly-Si films, such as low pressure chemical vapour deposition (LPCVD) (Harbeke 1983), crystallization by rapid thermal process (RTP) (Bonnel 1991) and solid phase crystallization (SPC) (Matsuyama 1990). However, in these techniques high temperatures are needed either during the film growth or in post-annealing processes which represent a drawback to obtain poly-Si films on glass substrates.

This work deals with the growth of poly-Si films by the hot wire chemical vapour deposition (HWCVD) method using a mixture of silane and hydrogen. By this technique poly-Si films with good electronic properties can be obtained at low growth temperatures (<500°C) and high deposition rates, also avoiding the need of post-annealing treatments (Matsumura 1993). The aim of this paper is then to asses the usefulness of the HWCVD method for the growth of poly-Si films from the scanning (SEM) and transmission electron microscopy (TEM) characterizations of the crystalline quality of these films. The results of other complementary characterization techniques as X-ray diffraction (XRD), Raman spectroscopy and Secondary Ion Mass spectroscopy will be also commented on.

2. EXPERIMENTAL

The films were grown on fused silica substrates in a hot-wire reactor from a mixture of 10 % silane - 90 % hydrogen. The reaction gases were activated by a tungsten filament, 1 mm thick and 150 mm long, that covered the whole sample surface homogeneously. The temperature of the filament was set to 1600 °C as measured by an optical pyrometer. The substrate temperatures were varied in the range 280-500 °C by placing the sample holder at different distances from the hot tungsten wire. The substrate temperature was measured by a calibrated thermocouple attached to the substrate holder. In

all experiments the total pressure was 21 Pa and the silane and hydrogen flows were 2 and 18 sccm, respectively.

The films were morphological and structural characterized by SEM, TEM, XRD and Raman Spectroscopy. For the TEM and TED analysis plan view and cross-section specimens were prepared. SIMS was used for the study of tungsten sample contamination during growth.

3. RESULTS

The study of the films showed the possibility of growing large columnar crystalline structures at moderate temperatures and high deposition rates and also the influence on these structures of the substrate temperature. No presence of tungsten contamination in the films was observed by SIMS.

The thicknesses of the deposited films were between 2 and 8 μm which correspond to values of growth rate as high as 40 Å/s. The increasing of the deposition temperature produced a decrease in the growth rate but even at the lowest substrate temperature (280 °C) the growth rate was very high (about 10 Å/s).

Small differences have been observed in the cristallinity of the films obtained. The XRD spectra of the samples showed the characteristic peaks of crystalline structures. The relative intensities of (111) (220) (311) (331) (422) diffraction peaks in the XRD spectra were similar. Moreover, when comparing these spectra with those of randomly oriented silicon, a (220) preferential orientation perpendicular to the substrate was observed in all samples. The crystalline character of the silicon films was also corroborated by Raman spectroscopy by the presence of an intense peak characteristic of poly-silicon centered al 520 cm^{-1} whereas no evidence of amorphous silicon was found.

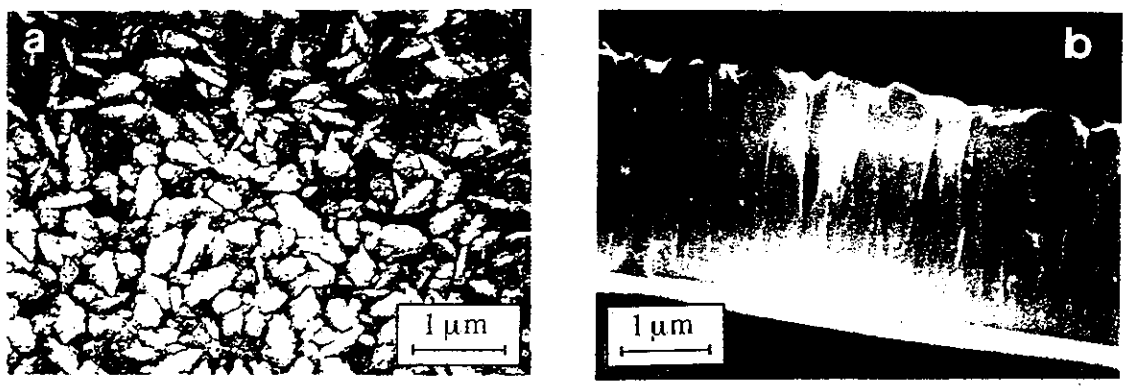

Fig. 1. SEM micrographs of surface (a) and cross section (b) for a sample deposited at 330 °C

The morphology of the poly-Si samples can be observed in the SEM micrographs of Fig. 1. Top views for all samples showed a structure formed by grains (Fig. 1a). The sample obtained at the highest temperature (500 °C) presented the largest grains with sizes ranging from 0.5 to 1 μm. The size of the grains decreased with the sample-filament distance. This effect could be attributed not only to differences in substrate temperature but also to the different thicknesses of the samples because of the columnar growth structure observed in the cross-sectional views (Fig. 1b).

A more detailed characterization of the poly-crystalline microstructure was carried out by TEM and TED analyses. Cross-sectional views (Fig. 2a) confirmed the columnar crystal growth already observed by SEM. The extension of the twin of the crystal shown in Fig. 2a allows us to outline the size of the crystalline columns which is larger than 1.3 μm. TED patterns of the cross section of the samples obtained from a selected area of 1μm diameter (inset in Fig. 2a) consisted of regular spots, whereas the diffraction rings, typical of polycrystalline material with small crystals, were not seen. Such diffraction patterns showing single-zone-axis reflections ([-111] zone axis) therefore corroborated the growth of films with large silicon crystals at moderate deposition temperatures (< 500 °C).

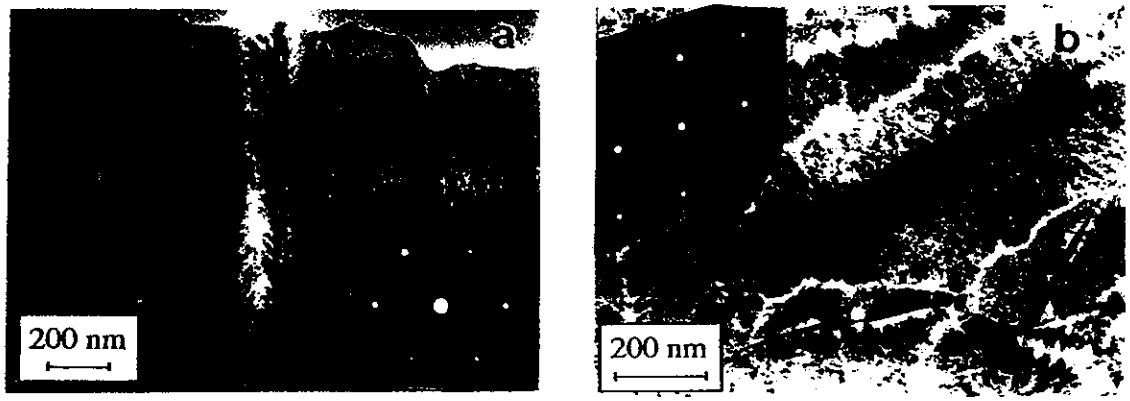

Fig. 2. TEM bright-field micrographs of silicon grains viewed along the [-111] direction in a XTEM view (a) and along the [110] direction (b) of a sample grown at 400 °C. The insets show the diffraction patterns.

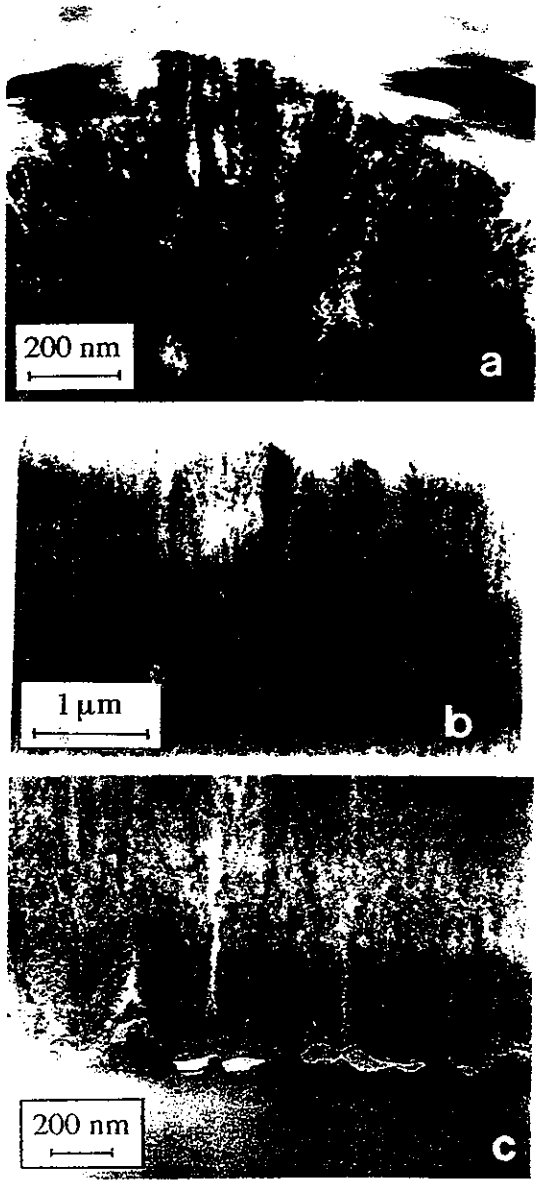

Fig. 3. Cross-section view of the crystal along all the film thickness.

In order to find out the growth direction of the crystals, a plane-view TEM study was performed (Fig. 2b). Needle shaped crystals ranging from 0.3 to 1 µm in length were found in the middle of the grains seen in the SEM images (corresponding to the white areas of Fig. 1a) and they were surrounded by a nanocrystalline material. Nanodiffraction patterns of most tested crystals showed a [110] orientation (inset in Fig. 2b) in agreement with the results of XRD. Moreover, nanodiffraction patterns obtained along the length of the crystals always showed the same zone axis [110], wich confirmed monocrystallinity of the grains.

Figure 3 shows that the monocrystal nuclei of the grains extended from the interface (Fig. 3c) across all the thickness of the poly-Si films (Fig. 3b) up to the top of the film (Fig. 3a).

Figure 4 illustrates the effect of the temperature on the film morphology. An increase of the crystal sizes was observed when increasing the deposition temperature. In these images it is also observable that the poly-Si grains are not perfectly compact. They are surrounded by very porous grain boundaries.

4. CONCLUSIONS

Morphological and structural studies performed with XRD, Raman spectroscopy, SEM, TEM and TED showed that poly-Si films could be obtained in a hot-wire CVD reactor when silane diluted in hydrogen was used as gas precursor. A columnar crystalline structure with 0.3-1 µm was observed with preferential orientation in [110] direction. In all polycrystalline samples, crystals columns extended from the substrates to the top of the films. The growth rate of poly-Si films ranged from 10 Å/s to 30 Å/s.

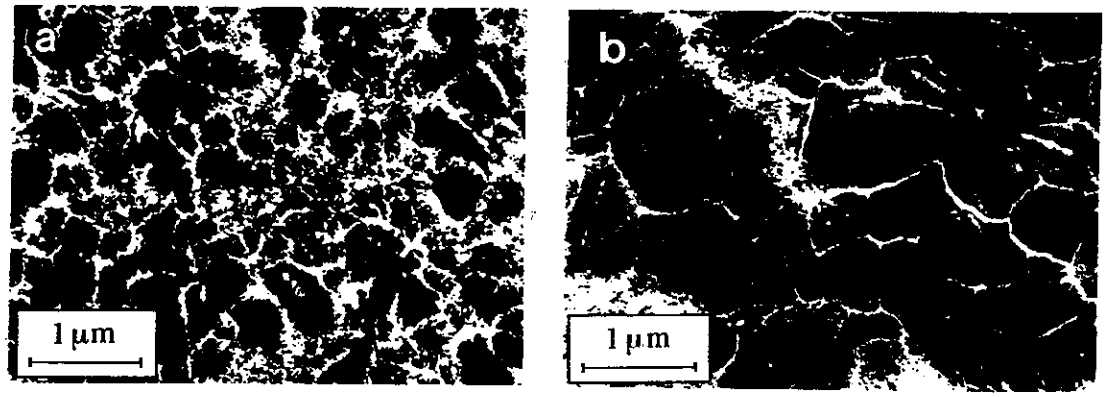

Fig. 4. TEM bright-field images of poly-Si samples deposited at 280 °C (a) and 400 °C (b).

These features associated with the high deposition rates and the scaling up possibilities make hot-wire CVD a very promising method for large thin film photovoltaic device development, for opto-electronic applications. Finally, we would like to point out the relevance of the presented results for the application of the obtained material on the fabrication of low cost, large area, poly-crystalline solar panels.

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