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COMMUNICATIONS

OPTICAL PROPERTIES OF RE–CRYSTALLIZED POLYCRYSTALLINE SILICON THIN FILMS FROM a–Si FILMS DEPOSITED BY ELECTRON BEAM EVAPORATION

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This paper deals with the structural and optical properties of the polycrystalline silicon films initially deposited in amorphous state by electron beam evaporation technology on a Corning glass and consequently thermally re-crystallized from solid phase. The re-crystallization process was "in situ" monitored by X-ray diffraction using an evacuated high temperature chamber at temperatures from 590 °C to 650 °C. Optical properties of the films carried out from the optical spectrophotometry recorded in a visible range of electromagnetic spectra were then confronted with the micro-structure parameters of the films. Relationships between the crystalline/amorphous composition, crystallite size, optical band-gaps and spectral extinction coefficients are clearly demonstrated.

K e y w o r d s: optical properties, a-Si thin films, annealing

1 INTRODUCTION

Polycrystalline silicon thin films are materials convenient for fabrication of photovoltaic cells of the 2nd and 3rd generation. Photovoltaic cells based on polycrystalline silicon thin films take advantage from thin film technology (material saving) and from well established silicon technologies (high quality material). Polycrystalline silicon thin films of a good quality can be prepared directly by CVD process at high temperatures (above 1000 °C) but it is necessary to use substrates, which are resistant to high temperatures (ceramics and suchlike) [1]. Another possibility how to obtain polycrystalline Si films of a good quality consists generally of two steps: (i) Deposition of a-Si or a-Si:H thin films by means of PVD or CVD technologies at low temperatures and (ii) subsequent recrystallization of the films from solid phase by thermal annealing at temperatures near to 600 °C. Despite simplicity and energy modesty this technology allows to use also the substrates, which are not resistant to high temperatures (Corning glass).

2 EXPERIMENTAL PART

Intrinsic amorphous silicon thin films of 2230 nm in thickness were deposited onto a Corning Eagle 2000 glass substrate by electron beam evaporation. Post deposition annealing of the samples (B11–B15) was performed in a high temperature chamber AP HTK 1200 at temperatures and periods indicated in Table 1. Physical properties of the films were investigated using X-ray diffraction (XRD), Raman spectroscopy and UV/Vis spectrophotometry.

Table 1. Parameters of the annealing process

Sample	Annealing temperature [°C]	Annealing duration [h]
B11-1	650	1.5
B11-2	600	1.5
B12-1	612	1.5
B13-1	590	1.5
B13-2	625	1.5
B14-1	590	3
B14-2	600	3
B15-2	590	6

XRD analysis of the films was carried out on an automatic X-ray powder diffractometer X'Pert Pro with a fast linear semiconductor detector Pixcel using an asymmetric (for amorphous state determination) and also a symmetric ϑ–ϑ geometry (for "*in situ*" measurements). CuKα radiation was used. XRD patterns were collected before, during ("*in situ*") and after heat treatment. Real structure analysis (size-strain) was performed using a procedure proposed by Langford [2]. A Jobin Yvon Labram HR Raman spectrometer equipped with a monochromator and a CCD detector was used to record the micro-Raman spectra at room temperature in the back-scattering geometry. The micro-Raman spectra were excited with a laser generating the wavelength of 532 nm. Raman mapping (Fig. 5) was carried out on all samples on the area of $350 \times 350\,\mu$m with a step of $50\,\mu$m. Laser spot was $1.5\,\mu$m in diameter. Evaluation of optical properties of the films was carried out on a UV/Vis spectrophotometer SPECORD 210 working in the wavelength range of

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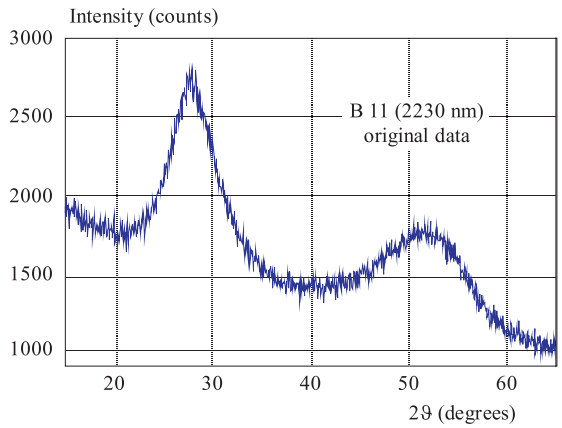

Fig. 1. XRD patterns for amorphous Si film recorded on a thin film attachment before annealing

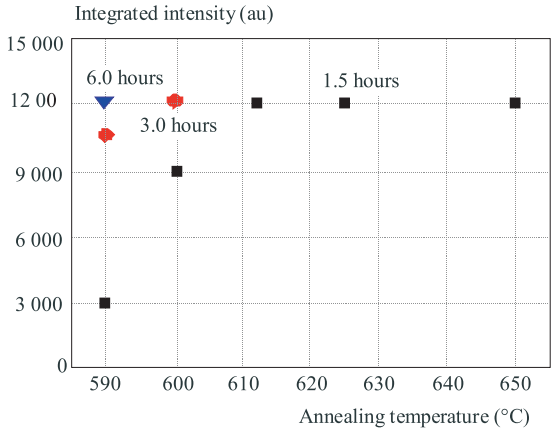

Fig. 2. XRD patterns for re-crystallized Si film recorded on a ϑ–ϑ geometry after annealing

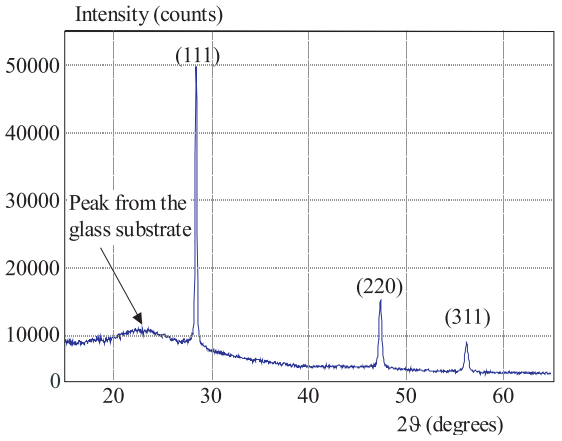

Fig. 3. Dependence of integrated intensity of (111) Si line on annealing temperature

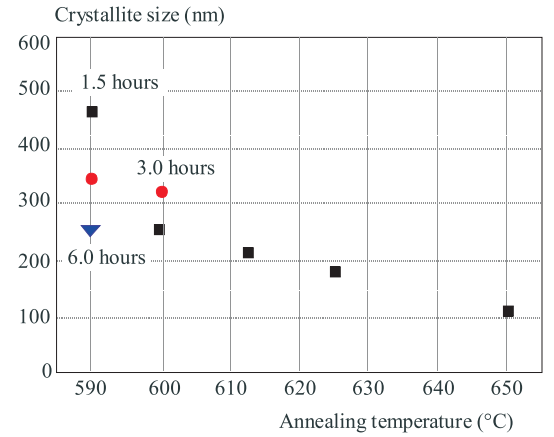

Fig. 4. Dependence of crystallite size on annealing temperature

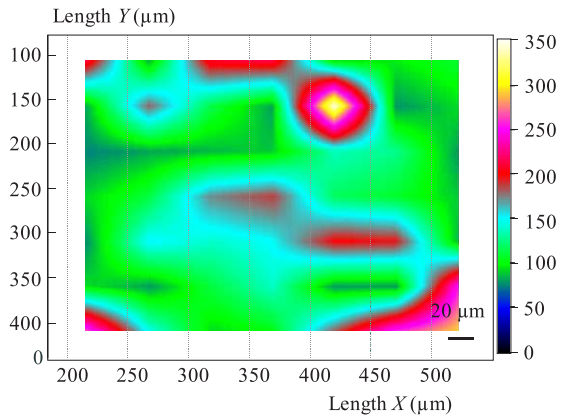

Fig. 5. Raman spectra map of film annealed at 590 °C for 1.5 hours

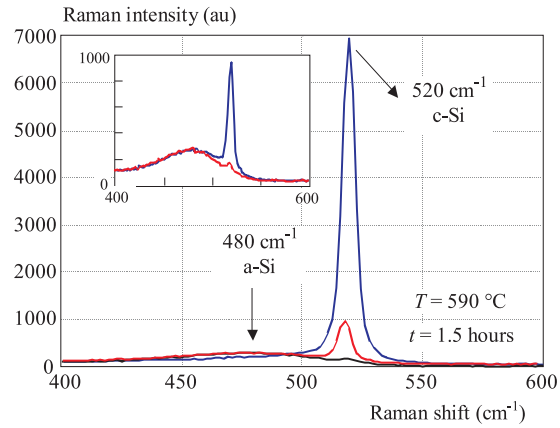

Fig. 6. Raman spectra of film annealed at 590 °C for 1.5 hours taken from three different places

190–1100 nm. Integral transmittance of the films was calculated in the range of 400–100 nm. To obtain optical band gaps, the Tauc's procedure was used [3, 4].

Initial amorphous and terminal fully crystalline states are presented as XRD patterns in Fig. 1, 2. XRD analysis indicated that crystallinity (polycrystalline-amorphous phase ratio) of the films and the resultant crystallite size (in direction perpendicular to sample surface) depends on annealing temperature and annealing duration (Fig. 3, 4).

Integrated intensity of a diffraction line expresses the volume ratio of a certain phase. In our case the integrated intensity of the (111) silicon line can be used as a measure of volume fraction of polycrystalline phase. As can be seen in Fig. 3 all films which reached the integrated intensity 12, 000 a.u. are fully polycrystalline.

The crystallinity of the films can also be determined using Raman spectroscopy. Fig. 6 shows Raman spectra from the films initial amorphous after annealing at temperature of 590 °C with duration of 1.5 hours. This fig-

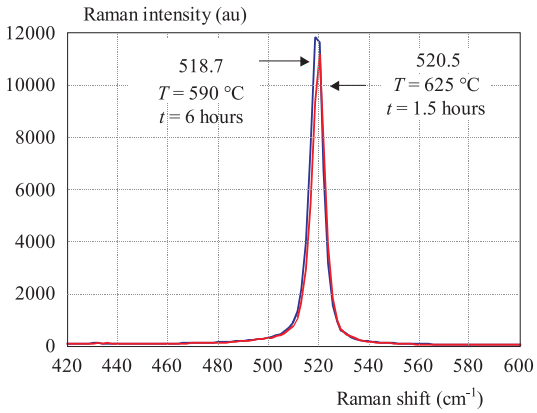

Fig. 7. Raman spectra of films annealed at 590 °C for 6 hours and 625 °C for 1.5 hours

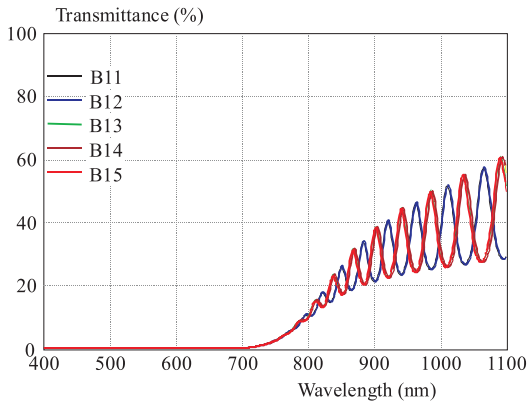

Fig. 8. Transmittance spectra before annealing (amorphous films before annealing)

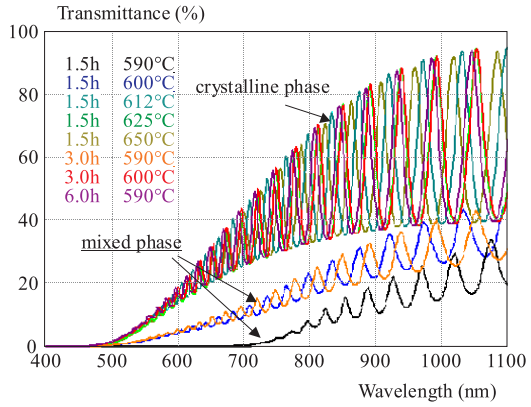

Fig. 9. Transmittance spectra for terminal state (after annealing)

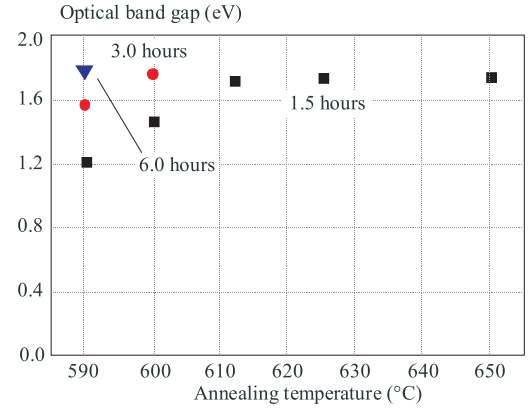

Fig. 10. Dependence of band-gap on annealing temperature

Table 2. Optical parameters

Sample	Integral transmittance (%)	
	Direct transition	Integral sphere
B11 initial	14.7	15.2
B11-1	35.8	37.1
B11-2	16.4	28.0
B12-1	35.8	37.3
B13-1	8.0	18.7
B13-2	35.0	36.4
B14-1	16.0	28.0
B14-2	35.3	37.1
B15-2	35.5	36.9

ure demonstrates differences in the structure and shows the presence of the crystalline and amorphous phase as well. Transverse optical (TO_n) mode of silicon can be divided into two parts: TO_1 branch with a peak position at 480 cm^{-1} from a-Si and TO_2 mode at about 520 cm^{-1} from c-Si. With increasing annealing temperature and duration there is a change of structure *ie* decreasing the share of amorphous phase and c-Si peak shifts toward shorter wave numbers (Fig. 7).

UV/Vis spectroscopy delivers information about transmittance of the films before (Fig. 8) and after annealing (Fig. 9), integral transmittance in the range of 400 to 1100 nm wavelength (Tab. 2), optical band gaps (Fig. 10) and extinction coefficients (Fig. 11) of the films. All this parameters depend on annealing temperature and annealing duration as well. As can be seen from Tab. 2 and Fig. 3, 9, 10, 11, structural and optical properties have some similarities. Regardless the crystallite size, fully crystalline films have almost the same structural parameters and also almost the same optical parameters.

3 DISCUSSION

Taking into account the microstructure parameters of the films carried out from the XRD analysis, the investigated samples can be divided into the three groups containing: (i) initial (amorphous) phase, (ii) mixed (amorphous and polycrystalline) phase and (iii) fully polycrystalline phase. It can be demonstrated in Fig. 1, where XRD patterns of amorphous state is presented and in Fig. 2, where XRD patterns of re-crystallized state is presented. Integrated intensities of the (111) diffraction lines for the films with different annealing conditions are presented in Fig. 3. Similar situation can be seen in Figures 8, 9, where transmittance optical spectra for the same films are reffered-to. To obtain fully re-crystallized films it is necessary to use annealing temperature at least 590 °C with annealing time of 6 hours. Using higher temperature the annealing time decreases. Otherwise the films are not fully re-crystallized (Fig. 3). Nevertheless, the highest average crystallite size of fully polycrystalline film was observed at annealing temperature of 600 °C with annealing time of 3 hours (Fig. 4). Fully re-crystallized films are homogeneous as confirmed also by Raman spectroscopy (Fig. 7) and they have almost the same optical properties (Fig. 9, 10, 11 and Tab. 2). Films annealed at lower

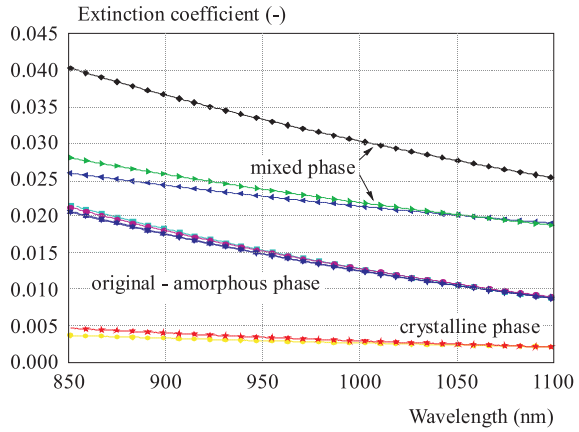

Fig. 11. Spectral extinction coefficient for a-Si films with different crystallinity.

temperatures and shorter times (590 °C for 1.5 or 3 hours and 600 °C for 1.5 hours) were not fully re-crystallized as confirmed by Raman and UV/Vis spectroscopy (Fig. 3, 5, 6 and 9). Although, they contain both amorphous and polycrystalline phases the crystallite size of their polycrystalline phase in average is higher than those fully re-crystallized films (Fig. 4). They contain both amorphous and polycrystalline phases, they are strongly inhomogeneous (Fig. 5, 6). As mentioned above, the investigated samples can be divided into the three groups, which observed not only by structural properties but also by optical properties (Tab. 2 and Fig. 10, 11). As can be seen in Fig. 11 the samples with mixed phase have higher extinction coefficient than other samples. Generally, the extinction coefficient is associated with absorption properties of the material. But in our case the lower transmittance is not caused by the absorption but it is caused by the dispersion of light on quite large crystallites build in the amorphous matrix which has higher refractive index than the polycrystalline phase.

4 CONCLUSIONS

The paper deals with utilization of XRD, Raman and UV/Vis spectroscopy to characterize physical properties of polycrystalline Si films obtained from a-Si films by means of solid phase re-crystallization, which seems to be a promising technology to obtain suitable material for thin film silicon solar cells. Regarding similarities between the structural experiments and the optical experiments we would like point out that optical spectroscopy is a powerful tool giving quick information compatible with the experiments obtained from structural analysis.

From the performed analysis point of view the optimal re-crystallization process seem to be that contains annealing temperature of 600 °C and annealing time of 3 hours. Nevertheless, also the processes giving not fully polycrystalline films can be utilized for tandem solar cells technology, because due to the light dispersion on the crystallites (optical in-homogeneities), the light path is much longer than in homogeneous materials.

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