Short thermal annealing for crystallization of plasma-cvd amorphous silicon films

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The possibility of obtaining acceptable crystallization time and high-quality poly-Si by using PECVD deposited amorphous silicon films with silane has been explored. The film structure has been investigated by x-ray diffraction and Raman spectroscopy as a function of annealing temperature. For samples annealed only 10 minutes, we found a sharp conductivity increment of about tree orders of magnitude for temperatures near and above 780°C. The x-ray diffraction for samples treated at 850°C, clearly shows crystalline phases along the <111>, <220> and <311> Si crystallographic directions in the case both c-Si and quartz substrates. This means, despite the short thermal annealing time, that the formed poly-Si textures are very similar to those made utilizing long-time crystallization procedures.

1. Introduction

The use of poly-Si (polycrystalline silicon) thin film devices on different substrates has been widely studied for diverse applications for a good number of years. Thin film solar cells are one of the attractive areas of applicability for poly-Si [1]. Many polycrystallization research activities have been carried out on films grown on glass substrates using, for example, by LPCVD (low-pressure chemical vapor deposition) [2]. In most of the Si crystallization cases, the sample is annealed during several hours at temperatures of the order of 600°C, which is below the glass substrate softening point. For example, research has been carried out on the effects on the crystalline structure of annealing temperature and time [3] and substrate-film interfacial properties [4]. However such long crystallization times for Si films constitutes a serious drawback for practical device mass production processes. More recently, the development of high temperature stable glass, extended the range of silicon deposition temperatures from a temperature regime of about 600°C to around 1000°C [5,6]. In this work, we have examined thin film poly-Si material properties fabricated by combining short and high temperature processes. A brief summary on sample preparation is as follows: the samples were prepared on quartz and polished c-Si (crystalline-silicon) substrates. Subsequently the samples were annealed for10 minutes at a temperature in the 760 to 850°C range. We report here the structural, optical and electrical properties of the annealed poly-Si films. These studies have been carried out by XRD (x-ray diffraction), Raman spectroscopy and a standard experimental set up to measure resistivity.

2. Experimental Details

Samples were prepared using SiH_4 (10% in H_2) as a source gas and PH_3 (1% in H_2) for obtaining n-type a-Si: H (hydrogenated amorphous silicon) material in a conventional capacitively coupled vertical plate PECVD(plasma-enhanced chemical vapor deposition) system. About 1μm thick a-Si: H films were deposited on both, 1 x 1 cm^2 quartz, and <111> oriented polished c-Si substrates at 250°C. The deposition rate was about 18nm/min. Film deposition conditions are described in table I. The thickness was determined by Talystep (Sloan Dektak IIA) measurements.

The crystallization process was done by a conventional thermal annealing process using a horizontal furnace with a continuos N_2 gas flow. The annealing temperature was varied from 760 to 850°C, while the annealing time was fixed to 10 minutes in all cases. The structural characteristics were investigated in both c-Si and quartz substrates by XRD (Siemens D5000) with a thin film attachment to avoid looking at the substrate. Additionally Raman spectroscopy measurements were performed at room temperature in a system with a double

Table I. Plasma-CVD deposition conditions for a-Si thin film.

Chamber pressure	1.0 Torr
RF power density	100 mW/cm^2
SiH_4 (10% in H_2)	50 sccm
PH_3 (1% in H_2) for n-type	5 sccm
B_2H_6 (1% in H_2) for p-type	5 sccm
Deposition time	60 min.

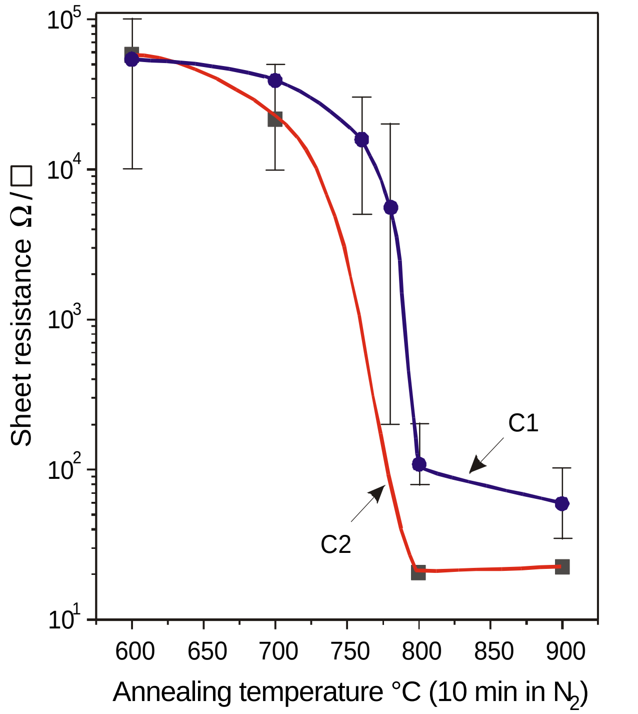

Fig.1. Sheet resistance as a function of annealing temperature for samples prepared on c-Si substrates. (C1) n-type and (C2) p-type materials.

monochromator and a photomultiplier used as detector. The films were excited with the 514.5 nm or 488.0 nm line of an argon ion laser. Hall effect measurements were also performed using Van der Paw's method. Optical transmission data were obtained in a double grating spectrophotometer (Shimadzu UV-2401PC) from which the optical enery band gap was calculated by means of the procedure described in Ref. [7].

3. Experimental Results

Sheet resistance-Annealing temperature

Fig. 1 shows Rst (sheet resistance) as a function of annealing temperature of the samples prepared on c-Si substrate. The sample C1 was prepared using phosphine as a doping source to form n-type material. In Fig.1, a steep Rst reduction of the sample for annealing temperature above 700°C is observed. This is related to a crystallization process of the deposited a-Si: H layers; further temperature increments may culminate this crystallization process achieving saturation. The crystallization activation temperature of sample C1 is around 780°C. this could be related to the accommodation of the micro twins absorbed by larger twins present in the sample [8]. In the same figure, C2 shows the characteristics of boron-doped samples annealed at different temperatures. In both samples, the abrupt conductivity changes seem to be promoted by the

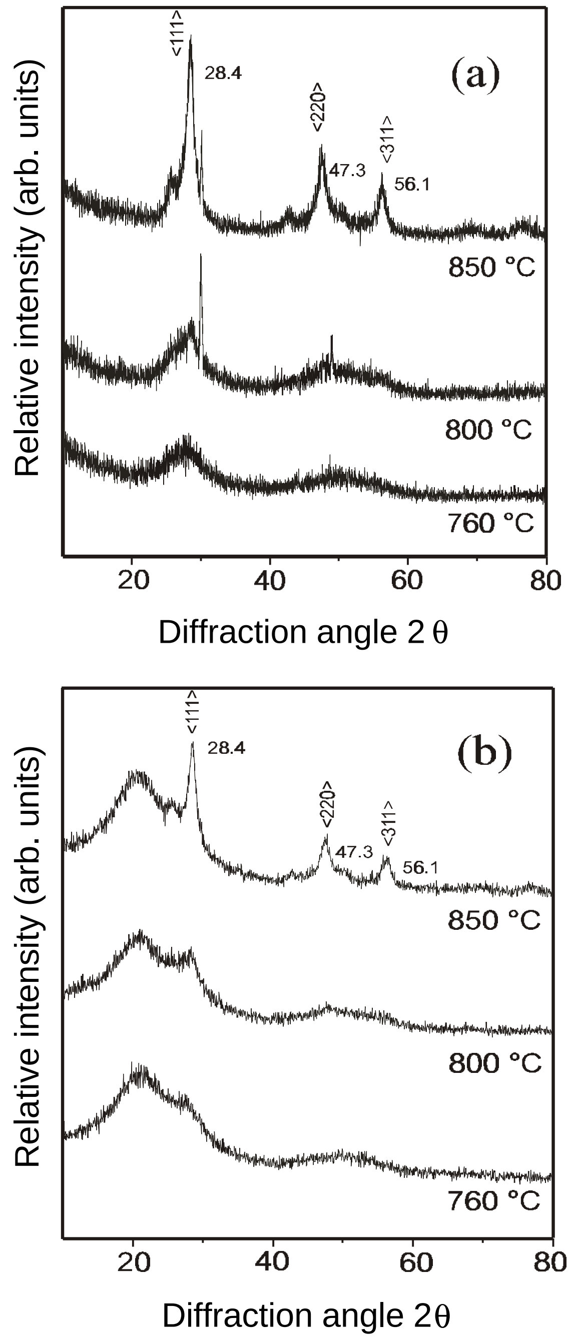

Fig.2. XRD spectra of the samples prepared on (a) c-Si and (b) quartz substrates for different annealing temperatures.

saturated crystallization from the quartz/a-Si: H interface towards the surface [9,10].

X-Ray Diffraction

A series of samples were prepared by PECVD employing quartz and c-Si substrates with the deposition condition described in table I. After deposition of phosphorous doped samples, each of both c-Si and quartz substrate samples were annealed at 760, 800 and 850°C during 10 minutes. XRD patterns of the samples made on c-Si (a) and quartz substrates (b) are shown in Fig. 2. XRD patterns of the materials deposited on both quartz and c-Si substrates annealed 10 minutes at 850°C, shows clear crystalline phases with <111>, <220> and <311> peaks. This means, in spite of the short thermal annealing time, that the formation of poly-Si crystalline textures are very similar in either c-Si or quartz substrates. These crystalline directions are similar to those observed in samples prepared by other techniques as low-pressure CVD [2] and RTP (Rapid thermal processing) annealed samples [11]. However, despite the appearance of crystalline peaks in both substrates, the silicon film formed on quartz substrate still shows an amorphous phase related shoulder, which could be the difference introduced by the substrate.

Raman-Spectroscopy

Fig.3 shows the room temperature Raman spectra for samples prepared on c-Si and quartz substrates. The spectra for the sample prepared on c-Si (a) reveals a clear peak at 520 cm^{-1} for each of the samples annealed from 760°C to 800°C. For comparison, it is also shown the Raman spectrum of a sample grown on c-Si substrate but
without annealing. On the other hand, for the samples prepared on quartz substrates (b) not well defined peaks appear at the annealing temperature of 760°C, showing only a broad band corresponding to an amorphous phase. However, for the sample annealed 800°C, a clear peak appears at 520 cm^{-1}, but as can be seen, still remains partially an amorphous phase. This means that the transition from an amorphous to a crystalline phase for samples deposited on quartz substrate takes longer times than those on c-Si.
Hall effect measurements reveal a carrier concentration of the order of $1.8x10^{19}$ cm^{-3} and a mobility of around 50 cm^2/vs.

Optical-Transmittance

Fig. 4 shows optical transmittance spectra of samples deposited on quartz substrates and annealed at 760 and 850°C. The sample annealed at 760 ºC (a) has greater transmittance than the sample annealed at 850°C (b) due to its amorphous phase perseverance. The calculated E_{gopt} (optical band gap) of the sample (a) was estimated around 1.37 eV, with a refraction index of 3.5, while for the sample (b), its E_{gopt} was around 1.09 eV, which is similar to c-Si. The measured transmittance spectra for both of the samples are concurrent with the Raman spectra shown in Fig.3.

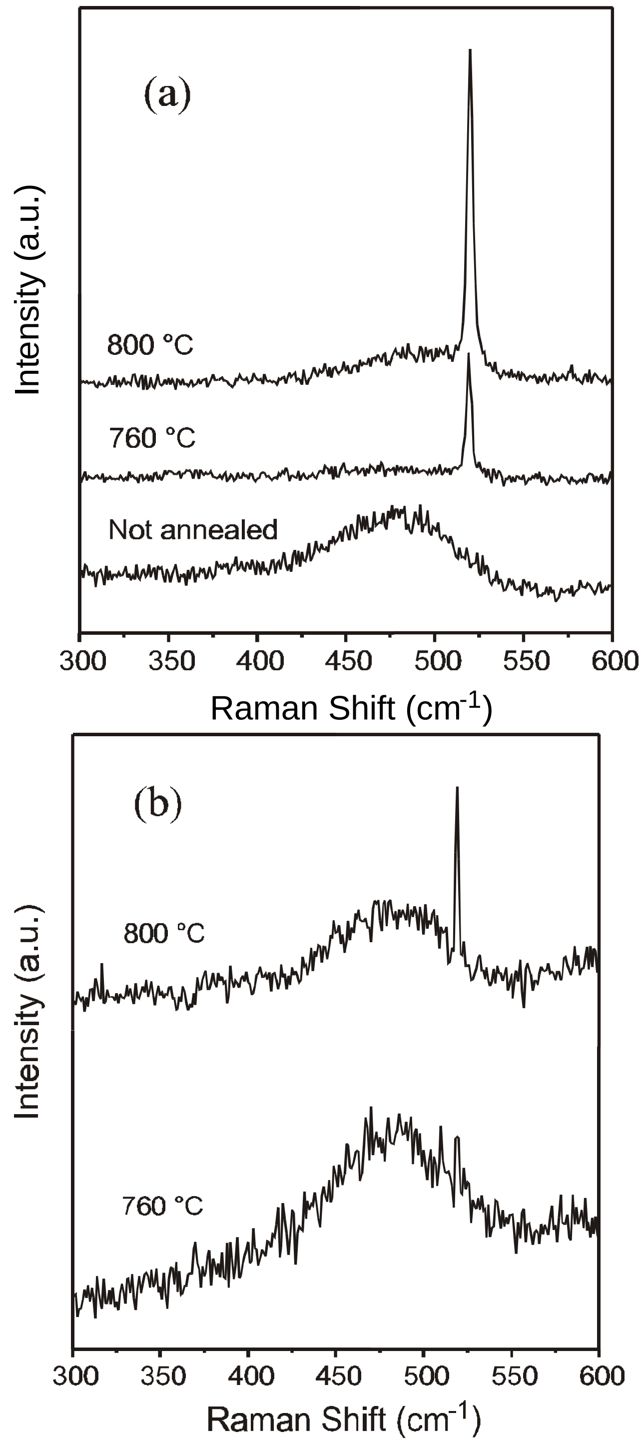

Fig.3. Raman spectra of the samples prepared on (a) c-Si and (b) quartz substrates.

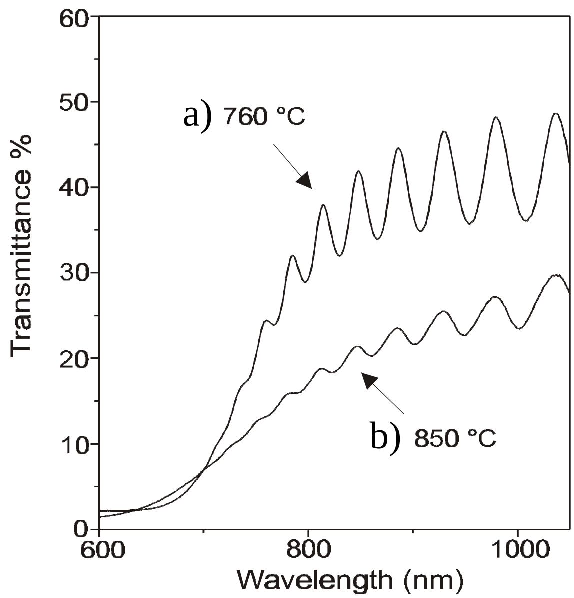

Fig.4. Optical transmitance of the samples deposited on quartz substrate and annealed at 760°C and 850°C during 10 minutes.

4. Conclusions

Thermal annealing polycrystallization of plasma-CVD deposited thin film amorphous silicon on quartz and crystalline silicon substrates have been studied. The sheet resistance changes drastically in the interval between 760 and 780°C, for 10-minute annealing processes. The XRD patterns reveal some crystalline orientation preferences which are the same for both quartz and c-Si substrates. However, a comparison of the Raman spectra between films deposited on quartz and c-Si substrates, shows a slower transition from amorphous to crystalline phase for quartz substrates.

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