Thin Solid Films 551 (2014) 181–187

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Polysilicon thin films fabricated by solid phase crystallization using reformed crystallization annealing technique

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ARTICLE INFO

Article history:
Received 2 May 2013
Received in revised form 22 November 2013
Accepted 22 November 2013
Available online 1 December 2013

Keywords:
Polycrystalline silicon
Solid phase crystallization
Quartz substrate
Annealing technique

ABSTRACT

In this work, a reformed crystallization annealing technique is presented for the solid phase crystallization (SPC) of amorphous silicon (a-Si) on SiN_x-coated quartz substrate. This technique includes a two-step annealing process which consists of a low-temperature (475 °C) classical furnace annealing for nucleation of Si and a high-temperature (900 °C) grain growth process of polycrystalline silicon (poly-Si) during thermal annealing in classical tube furnace. The aim of this reformed two-step annealing technique is reducing the long (up to 48 h) crystallization annealing duration of single step annealing at low temperatures (~600 °C) while maintaining the film quality, as low-temperature single step annealing, by using reformed technique. Continuous p-type poly-Si film was formed on quartz substrate thanks to exodiffusion of boron, which was deposited prior to a-Si, through Si film by thermal annealing. The stress and degree of crystallinity of the p-type poly-Si were studied by the micro-Raman Spectroscopy. The crystallization fraction value of 95% was deduced for annealed samples at 900 °C, independent from crystallization technique. On the other hand, the Raman analysis points out that compressive stress was induced by increasing the annealing duration at 900 °C. X-ray diffraction (XRD) analysis reveals that the preferred crystallite orientation of the films, independent from crystallization temperature and substrates, is <111>. Additionally, the average crystallite size calculated from XRD patterns increases from 69 Å to 165 Å by using reformed two-step annealing instead of single step annealing at 900 °C for 90 min. The exodiffusion of boron into the silicon film was deduced from secondary ion mass spectrometry (SIMS) analysis and the p^+/p graded boron profile was obtained, which may result higher carrier diffusion length and longer carrier life time. Finally, the annealing duration dramatically decrease to 9 h by using reformed two-step annealing technique instead of conventional single step annealing at 600 °C. The results show that reformed SPC annealing technique has major advantages by combining the lower annealing duration and high crystal quality.

1. Introduction

Thin-film approaches aim to reach low cost by starting with a low-cost material system; a thin layer of semiconductor is deposited on a low-cost substrate. Thin-film polycrystalline silicon (poly-Si) solar cells on foreign substrates combine the advantages of crystalline silicon and thin film technology, and become a promising alternative to bulk silicon solar cells due to their low cost, high quality and large-area applications. Relatively large grain size and high crystalline fraction are the other main advantages of the polycrystalline silicon thin films. Among the various techniques for the formation of poly-Si on a foreign substrate, solid phase crystallization (SPC) [1] of amorphous silicon (a-Si) is a way for the high efficiency poly-Si based cells with 10.4% efficiency [2]. The advantages of using SPC of a-Si are that it is simple and cost-effective, and produce a relatively high-quality silicon layer as well as its ability to produce a smooth interface and excellent uniform film with a high reproducibility [3,4]. The grain enhancement in this process results from a movement of grain boundaries (GBs) activated by the heating. An increase in the time or temperature, or both, can further promote the grain growth. Typically the amorphous silicon films are between 1 and 3 μm thick, and can either be undoped, moderately doped or highly doped, or consist of multiple layers with different doping levels. After deposition, the films are annealed at temperatures between 550 and 700 °C, for a long period of time, typically several tens of hours. The higher the temperature, the faster full crystallization will be reached, but the smaller the grains will be. If the temperature is too low, full crystallization is not reached within a reasonable time. A workable compromise is 600 °C [5–7]. Although SPC has several advantages, the major drawback of the thermal annealing process is that it requires a long time. A typical annealing process will take 24 to 48 h to ensure the formation of poly-Si films with large grain size, making it uninteresting for fabrication [4,8,9].

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0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2013.11.098

In this study, a reformed two-step annealing is proposed to transforms the a-Si to poly-Si films for the fabrication of high quality poly-Si thin films by SPC technique in shorter time compared by conventional single step annealing duration (24–48 h). The first step of reformed technique is the low-temperature annealing at 475 °C for 8 h in tube furnace which is a classical thermal process (CTP) to start the nucleation of Si with a lower nucleation rate to increase the crystallite size, which is followed by high-temperature annealing at 900 °C in the range of 30 min to 90 min in CTP to reduce the annealing time dramatically by reducing the grain growth duration. The aim of reformed two-step annealing technique for SPC process is to significantly reduce the crystallization annealing duration and improve the crystal quality by combining the advantages of annealing at low temperature (475 °C) and high temperature (900 °C). It turns out that poly-Si thin films fabricated with the reformed two-step annealing technique not only lower the crystallization duration as compared to those fabricated by conventional annealing at low temperatures (~600 °C) but also possess large crystallite sizes as similar to obtained in conventional annealing at low temperatures (~600 °C). Additionally, it should be noticed that two-step annealing results the enhancement in crystallite size compared with single step annealing process at 900 °C.

In this paper, we investigate the formation of p-type polysilicon thin films on quartz substrate by using the SPC process with two-step annealing technique. The SPC technique that consists of intrinsic a-Si deposition by electron beam (e-beam) evaporation system and ex-situ annealing for the crystallization using a CTP is used to form the continuous p-type polysilicon films. The intrinsic a-Si is transformed into a p-type polysilicon film by thermal exodiffusion of boron from a solid source, evaporated onto the SiN_x-coated quartz, into the deposited a-Si layer during thermal annealing process in classical tube furnace. The stress and degree of crystallinity of the p-type poly-Si films were studied by the micro-Raman Spectroscopy. The preferential orientation and average crystallite size of the resulting p-type films are deduced from the X-ray diffraction (XRD) technique. Four point probe measurement was accomplished to obtain the resistivity of the films and corresponding carrier concentration was calculated. Secondary ion mass spectrometry (SIMS) analysis was used to analyze the doping profile of boron diffused from solid boron source into Si film.

2. Experimental details

Quartz with the thickness value of 1 mm was used as a substrate for the high temperature applications (≥900 °C). Additionally, quartz allows the superstrate configuration for solar cell applications due to its transparency. Prior to film formation, an 85 nm thick SiN_x was coated on quartz substrates by plasma enhanced chemical vapor deposition (PECVD) system. SiN_x thin film was deposited in a cluster chambered PECVD which was designed by VAKSİS Ltd.. The deposition was performed in capacitively coupled plasma type chamber. The substrate temperature was 200 °C and the power was 100 W during the deposition. As the precursor gases, ammonia (NH_3) and silane (SiH_4) were used with a ratio (NH_3/SiH_4) of 2 with the deposition rate of 5.6 Å/s. SiN_x thin film is a good candidate as a barrier layer for potential contaminations (O, B, Na, K, Al, Fe, etc.) that can diffuse from the quartz substrate into Si film during annealing processes [10]. To use as a dopant source for following intrinsic a-Si layer and obtain a p-type poly-Si, boron was deposited on SiN_x-coated quartz by e-beam evaporation system from a high purity B powder (99.9999%). The homogeneity of the deposited films is supplied by the rotating holder during the evaporation. A 25 nm thick boron film was deposited on all samples at a deposition rate of 0.7 Å/s. The boron film deposition conditions are defined as substrate temperature of 200 °C, emission current of 70 mA, voltage of 8.5 kV and base pressure of 1–2 $\times 10^{-4}$ Pa. Without taking out the sample from e-beam evaporation system's chamber, boron deposition was directly followed by the evaporation of high purity intrinsic a-Si by using the same e-beam evaporation system. The crucible heart was changed for silicon evaporation. The advantage of using the e-beam evaporation system for a-Si deposition is that a hydrogen free a-Si film which is very important in device applications with limitation of H-related impurities can be formed. Before the deposition of a-Si, the chamber was evacuated to a base pressure of 1.33×10^{-4} Pa–2.66×10^{-4} Pa. An a-Si layer with a thickness of around 1 μm film was deposited. The deposition rate of evaporation system and the substrate temperature were 4–5 Å/s and 200 °C, respectively, which were stable during a-Si deposition. During the deposition the current emission was changed between 60 and 65 mA to maintain a stable deposition rate while the value of voltage was 8.5 kV. The quartz/SiN_x/boron/a-Si structure was isothermally annealed by CTP for solid phase crystallization (SPC). The annealing process was accomplished under N_2 flow in furnace. The tube furnace with one zone was product of PROTHERM Ltd. which contains high resistances around in the middle of the quartz tube. The annealing zone of the furnace has quite stable temperature during annealing process. After SPC annealing, continuous poly-Si films were formed on SiN_x-coated substrate. The aim of ex-situ CTP annealing is the crystallization of a-Si for SPC technique while the exodiffusion of boron into silicon layer was achieved in parallel during this ex-situ annealing. In this work, we tested the effect of crystallization annealing on the structure of poly-Si. While we were using the single-step crystallization annealing which was at 900 °C for 90 min, we also used the reformed two-step annealing which includes 475 °C for 8 h and 900 °C for 30 min, 60 min and 90 min. All these annealing processes and the name of samples are summarized in Table 1.

The thickness of the films was measured by DEKTAK profiler which uses a probe that scans the surface and makes the measurement with respect to the step that is accomplished by the deposited film. The crystallinity of annealed samples was studied by using micro-Raman spectroscopy which is HR 800 Jobin Yvon attached with Olympus microanalysis system and a charge-coupled device camera providing a resolution of 1 cm^{-1}. The spectra were carried out in backscattering geometry with the 632.8 nm line of He–Ne laser at room temperature. In addition to crystallinity, the stress level of poly-Si films was also determined by Raman analysis. The crystal orientations and crystallite sizes of poly-Si films were identified by a Rigaku MiniFlex X-ray diffractometer with monochromatic CuKα_1 incident beam ($\lambda = 0.154056$ nm) operated at 30 kV and 15 mA. The scanning was accomplished between 10° and 90° 2θ values with a step of 0.02. The values of sheet resistance were deduced by using a Jandel RM3-AR four point probe system. The boron concentration profiles were analyzed by secondary ion mass spectrometry (SIMS) using an ION-TOF ToF-SIMS 5 system having Bi ion source with a power of 1 keV. During the SIMS sputtering, oxygen (positive) source was used. The calibration of the boron concentration was performed using a standard wafer implanted with a known boron dose.

3. Results and discussions

3.1. Raman analysis

Micro-Raman spectroscopy is a straightforward, sensitive, fast and useful technique for characterizing the structure of poly-Si thin films. Thus, Raman spectroscopy is used for monitoring the crystal quality

Table 1
Description of crystallization annealing durations for samples A, B, C, D and E.

Sample name	Annealing duration at 475 °C (h)	Annealing duration at 900 °C (min)
A	8	0
B	8	30
C	8	60
D	8	90
E	0	90