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Poly-Si films prepared by rapid thermal CVD on boron and phosphorus silicate glass coated ceramic substrates

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Abstract

This study investigates the crystallographic properties of polycrystalline silicon films formed on doped (boron or phosphorus) or undoped silicate glass coated ceramic substrates using the chemical vapor deposition method at high temperatures (>1000 °C). First, FT-IR analysis of the silicate oxide layers is presented in order to monitor the presence of the Si–O, B–O and/or P–O bonds in the layers prior to deposition. Then, the average grain size, crystalline orientation and boundary defects of these poly-Si films on silicate coated mullite and alumina were evaluated as a function of deposition parameters and boron/phosphorus content. The results show a significant increase of the grain size and narrower size distribution after CVD on BSG or PSG intermediate layers, whatever is the substrate. Large grains up to 7 μm are observed for 9 μm thick films. The enhancement in grain size is attributed to the nucleation change by defects or impurities rather due to the flowability of the silicate glass during the silicon deposition at high temperature. The open-circuit voltage measurements of these fine-grained poly-silicon films before hydrogenation shows a dependence on the grain size through the choice of the substrate. The open-circuit voltage increases substantially from 250 mV to 410 mV after 1 h plasma hydrogenation, despite partial etching of the emitter by the hydrogen atoms.

Keywords: Polycrystalline silicon; Chemical vapor deposition; Ceramics

1. Introduction

For solar cell applications, thin polycrystalline silicon films (<10 μm) on low-cost foreign substrates are a promising alternative approach to thick multicrystalline Si materials [1]. Most of the works report on polycrystalline Si films made by high temperature chemical vapor deposition (CVD) growth on bare ceramics like alumina, mullite, SiSiC and SiN [2–4]. Such poly-Si layers are characterized by small grains and a large number of grain boundaries, and dislocations that limits the electronic properties. Enlarging the grain size which is the most obvious way of decreasing the defect density is quite challenging. Among approaches to reach a grain size much larger than the layer thickness, there are methods such as the aluminium induced crystallization of amorphous silicon [5], the zone melting recrystallization of a seed CVD Si layer [6], the iodine vapor transport at atmospheric pressure [7] and the pulse-CVD process [8]. Another way to enlarge the grain size is to reduce the nucleation density in the initial stage of the CVD deposition. One might use a seed layer which is able to provide grains with very small aspect ratios. Graef et al. [9], employing what is called the CVD-OLL (CVD on Liquid Layer), have obtained layers with grain sizes up to 100 μm using sputtered Sn layers. This is explained as the result of the enhanced mobility of the Si-adatoms over the surface of this low-viscosity layer (the surface approaches the features of a liquid surface) and the ability of the Si-nuclei to rotate on this surface. The possible use of silicate glass films that become viscous at the temperature of Si CVD might be an interesting alternative to metals. Furthermore, the presence of phosphorus and boron impurities in silicate glass (PSG or BSG, respectively) is known to modify the viscosity [10,11].

In this study, we report on the crystalline and electronic properties of poly-Si films deposited by conventional atmospheric pressure CVD at temperatures above 1000 °C on

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ceramics coated with doped and undoped silicate glass layers. Oxidized silicon substrates were also used as a reference substrate. In the following such deposition process will be called CVD-OGL (CVD on Glassy Layer). The glass films were applied on the ceramic substrates using spin-coating and may act as an impurities barrier or even as a doping source. The grain size, distribution and crystallographic orientation of the poly-Si were determined by optical microscopy and electron backscattering diffraction measurements (EBSD). The electronic properties of the poly-Si layers were monitored through the open-circuit voltage measurements before and after plasma hydrogenation.

2. Experimental

Different silicate glass solutions were used: (i) FOx (Flowable oxide) solution is a Hydrogen Silsesquioxane Resin [HSQ: $(HSiO_{3/2})_n$] provided by Dow. It is very widely used for surface planarization in microelectronic industry; (ii) FOx-TQB for which boron was incorporated into the HSQ resin system, it will be denoted BSG; (iii) undoped (SOG, 700A) and (iv) phosphorus (PSG, P509) doped Spin-on glass (provided by Filmtronics Inc.). The PSG and BSG silicate glass solutions contain a concentration of phosphorus (15% P) and boron (8% B), respectively. A BPSG solution has been made by mixing the two solutions BSG and PSG on a 1:1 ratio basis.

The solutions were spun onto the ceramic substrates and then baked in oven at 210 °C for 20 min. This resulted in glassy layers (GL) with thicknesses in the range 0.6–1.1 µm and 0.3 µm for, respectively, Dow and Filmtronics solutions.

The ceramic substrates used in this work are alumina (Al_2O_3 from Coors) and two kind of mullites ($3Al_2O_3-2SiO_2$). The mullites fabricated by VITO (mullite-V) were made from pure mullite powder while the mullites fabricated by CIM (mullite-C) were obtained by mixing alumina and silicate glass powders. The mechanical properties of both mullites were adjusted by playing with the starting powder(s) to form the slurry as well as with the sintering temperature ($\geq$1500 °C), and were prepared by the doctor blade technique. The final composition defines the amorphous phase content and porosity. Both types of mullite ceramics were mechanically polished. Mullite-V presents very small grains and close pores while mullite-C exhibits large grains and some large open pores. The main advantage of the mullites is a thermal expansion coefficient very close to that of silicon, which makes it very compatible with high temperature processing.

The deposition process was carried out in a rapid thermal atmospheric pressure chemical vapor phase reactor (RT-APCVD) using 12 halogen lamps as heat source. Trichlorosilane of 1 g/min diluted in hydrogen was used as the precursor gas and the Si layers were in situ doped with boron from 5% trichloroborine gas source in H_2. Prior to the entrance of the reactive gas, an in situ cleaning at the deposition temperature is performed under hydrogen flow. A thin polycrystalline silicon p^+ layer is first deposited, followed by the active p layer. For both layers the deposition temperature is in the range 1050–1150 °C. The typical thickness for the deposited p^+ and p layers is 3 and 6 µm, respectively. The growth rate of these films is 3–4 µm/min. The CVD was performed on glassy coated ceramics as well as on bare ceramics and oxidized silicon (th-SiO_2) substrates. The th-SiO_2 ones serve as an "ideal" model of foreign substrates.

The open-circuit voltage has been measured on n^+pp^+ mesa structures. Thus a p^+–p structure was first deposited and the n-type emitter region was realized by conventional furnace from phosphorus doped spin-on glass source (P509). The thermal processing was carried out at 900 °C for 15 min resulting in a sheet resistance of about 25 Ω/□. Due to the insulating barrier layers, access to the base was possible by chemical etching around the cell, thus forming a 1×1 cm^2 mesa cell. Some samples received a plasma hydrogenation at 400 °C for 1 h using a remote plasma system (Roth-Rau).

3. Results and discussions

3.1. Analysis of the flowable oxide films

Fig. 1 plots the FTIR absorbance spectra for the used glass oxide layers after annealing at 1000 °C for 1 min in Ar. FTIR spectra were recorded using Bruker Optik spectrometer in transmission mode. Each FTIR spectrum was obtained as an average of 50 scans at 4 cm^{-1} resolution and background to a clean bare Si ⟨100⟩ wafer, as a reference. The FTIR analysis gives the structural properties of the glass layers prior to the high temperature silicon deposition. The thermal annealing induces composition changes from hydrosiloxanes to SiO_2. For all spectra, the SiO_2 matrix is identified by vibrations assigned to the symmetric O–Si–O rocking bond at 450–460 cm^{-1}, bending bond at 810–820 cm^{-1}, asymmetric Si–O stretch at 1075–1085 cm^{-1}, and the Si–O–Si stretch, which is a shoulder at 1190 cm^{-1}. The peak intensities are stronger for the FOx since the film is much thicker. Although quite weak, additional vibrational features can be observed on the spectrum of BSG at 930 cm^{-1} and 1395 cm^{-1} and are

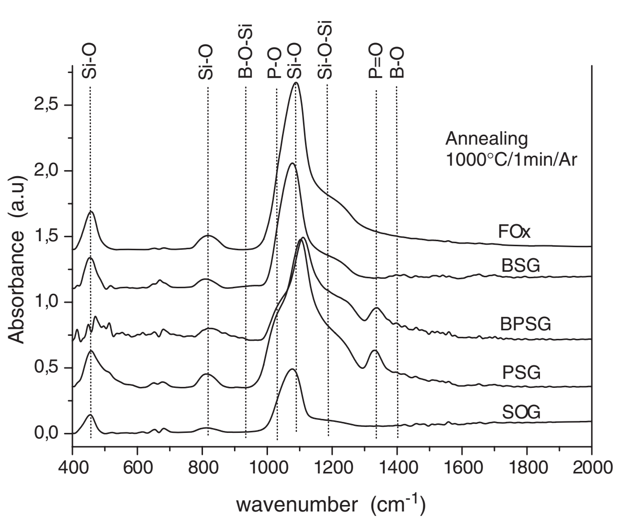

Fig. 1. Infrared absorption spectra of the used glass oxide layers. The solutions were spun on silicon, baked and then annealed at 1000 °C for 1 min under Argon. Except for FOx spectrum, other spectrum data are multiplied by 3.