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n-type Polycrystalline Si Thick Films Deposited on SiN_x-coated Metallurgical Grade Si Substrates

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For photovoltaic applications, low-cost SiN_x-coated metallurgical grade silicon (MG-Si) wafers were used as substrates for polycrystalline silicon (poly-Si) thick films deposition at temperatures ranging from 640 to 880 °C by thermal chemical vapor deposition. X-ray diffraction and Raman results indicated that high-quality poly-Si thick films were deposited at 880 °C. To obtain n-type poly-Si, the as-deposited poly-Si films were annealed at 880 °C capped with a phosphosilicate glass. Electrical properties of the n-type poly-Si thick films were investigated by four-probe and Hall measurements. The carrier concentration and electron mobility of the n-type poly-Si film was estimated to be 1.7×10^{19} cm^{-3} and 68.1 cm^2 V^{-1} s^{-1}, respectively. High-quality poly-Si thick films deposited on MG-Si wafers are very promising for photovoltaic applications.

KEY WORDS: Thermal chemical vapor deposition; Metallurgical grade Si; Polycrystalline silicon (poly-Si) thick films; Phosphorus diffusion

1. Introduction

Polycrystalline silicon (poly-Si) films have attracted attention for more than one decade because of their important applications in high-efficiency solar cells[1] and high-performance thin-film transistors[2,3]. Thermal chemical vapor deposition (CVD) has been proved to be an efficient method for preparing high-quality poly-Si films[4]. Since elevated temperatures (≥800 °C) are needed for high-quality poly-Si deposition, substrates should have a coefficient of thermal expansion (CTE) close to that of Si (4×10^{-6} K^{-1})[5] to avoid peeling off the as-grown silicon layers. Moreover, another important concern is out-diffusion of impurities from the substrate into the active layer during the deposition process for poly-Si deposition at high-temperature. Therefore, only a limited number of substrates are available, such as graphite, mullite, Al_2O_3, SiN_x, SiAlON and Al_2O_3−SiO_2[6−8]. Diffusion barriers such as SiN_x and SiO_2 are frequently deposited on these substrates to prevent substrate impurities from contaminating active layers[9−11]. For example, an 85-nm-thick SiN_x layer was used as the diffusion barrier in the prevent of poly-Si films on Al_2O_3 substrates by aluminum induced crystallization (AIC) method[8]. SiN_x-coated metallurgical grade silicon (MG-Si) substrates not only meet the CTE substrate requirements mentioned above, but also possess several advantages over other substrates, such as lower cost and a more mature fabrication process. Moreover, large-scale industrial production is feasible permitting a monolithic integration of MG-Si substrates[12]. However, the applications of the MG-Si substrates for the deposition of poly-Si thick films in photovoltaic applications have not been addressed yet.

Doping is essential to create the photo-active p/n junction. p-type boron treated at 1100 °C using BCl_3 as the doping source resulted in a minority carrier lifetime of 0.1−0.2 μs, a carrier concentration of 4.0×10^{17} cm^{-3} and a mobility of 69 cm^2 V^{-1} s^{-1}[13]. n-type doping of as-grown AIC poly-Si films was obtained using a highly phosphorus doped glass solution as the doping source at 1000 °C[8]. Such n-type poly-Si film has a Hall mobility of 25.4 cm^2 V^{-1} s^{-1} and an electron concentration of 5.9×10^{20} cm^{-3} n-type and p-type doping of the poly-Si films could be achieved at 1100 °C during rapid thermal CVD using phosphosilicate glass (PSG) and borosilicate glass intermediate layers as doping sources, respectively[14]. However, a high-temperature (≥1100 °C) is needed to obtain such p-type or n-type poly-Si films.

In this work, SiN_x-coated MG-Si wafers were used as the substrates for high-quality poly-Si thick films deposition. n-type doping was carried out by annealing the as-deposited poly-Si thick films at 880 °C using a PSG layer as the phosphorus source. An electron concentration of 1.7×10^{19} cm^{-3} and an electron mobility of 68.1 cm^2 V^{-1} s^{-1} were obtained for the n-type poly-Si films.

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2. Experimental

Fig. 1 shows the schematic diagram to fabricate undoped (Fig. 1(a)) and P-doped poly-Si thick films (Fig. 1(b)). First, a 350 nm-thick SiN_x films were deposited on the MG-Si wafers by plasma enhanced chemical vapor deposition (PECVD) at 400 °C at a pressure of ~30 Pa. The power was fixed at 100 W using a 13.56 MHz RF source. NH_3 and SiH_4 (90%Ar + 10%SiH_4) were supplied into the chamber as reactive gases at a flow rate of 8 and 12 sccm, respectively. Then, the poly-Si thick films were deposited at various deposition temperatures ranging from 640 to 880 °C on these SiN_x-coated MG-Si substrates by CVD furnace using SiH_4 and H_2 at a pressure of 2000 Pa. Rapid, uniform radiant graphite resistance heating elements were used for the sample holder and heater. Doping was carried out at ~880 °C under the background pressure of ~10 Pa. First, the as-deposited poly-Si thick films were put on top of the uniform flat graphite resistance heating elements. Then, PSG coated commercial solar Si wafers with the size of ~2 cm × 2 cm were put on top of the as-deposited poly-Si thick film in a face-to-face mode (Fig 1(b)). No intentional gap is provided between the PSG layer and the poly-Si thick film. At the high-temperature, a large amount of P atoms would out-diffuse from the PSG layer. Thus, the as-deposited poly-Si layer would be doped by the thermally activated P atoms, leading to the formation of the n-type poly-Si layer. For comparison, the poly-Si thick films were also fabricated by a solid-phase crystallization (SPC) process at 1000 °C using amorphous Si (a-Si) thick films deposited at 280 °C by PECVD from SiH_4 as the precursor.

The microstructures and the surface morphologies of the poly-Si thick films were analyzed by field emission scanning electron microscopy (FESEM, Hitachi S-4800 operated at accelerating voltage of 4 kV), X-ray diffraction (XRD, Bruker D8 Advance using Cu$K\alpha$ (λ = 0.15406 nm) radiation and a thelta−thelta configuration) and Raman spectra (the poly-Si thick films on fused silica substrates) (Renishaw inVia Raman Microscope exited at 488 nm by an argon laser), respectively. Electrical characteristics of the P-doped poly-Si thick films were measured by four-probe (NAPSON CRESBOX) and Hall measurements (Nanometrics HL5500PC). Microwave photoconductivity decay (μ-PCD) mapping was measured with a Semilab (WT-2000PVN) instrument with 904 nm excitation wavelength. Electrochemical capacitance−voltage (ECV) technique (Wafer Profiler CVP21) was used to characterize the doping profile of the n-type poly-Si thick films.

3. Results and Discussion

Fig. 2 shows cross-section (a) and top-view (b) SEM images of the poly-Si thick films deposited at 880 °C on the SiN_x-coated MG-Si substrate by thermal CVD. The cross-section of the stack films shows that the poly-Si films have a compact morphology with a thickness of up to 20 μm, as shown in Fig. 2(a). The particle size of the poly-Si film increases with increasing film thickness. The thickness of the SiN_x layer is determined to be about 350 nm as shown in the inset of Fig. 2(a). The surface morphologies illustrated in Fig. 2(b) are polycrystalline with an average particle size of up to a few microns.

Fig. 3(a) shows XRD patterns of the thermal chemical vapor deposited poly-Si thick films as a function of deposition temperature. By applying the Scherrer's equation, average crystalline grain sizes of the poly-Si thick films deposited at 640, 800, and 880 °C are calculated to be approximately 31.4, 37.2 and 68.4 nm from (111) peaks, respectively. The dominant crystal orientations are (111) and (220). Fig. 3(b) shows the Raman scattering spectra of the as-deposited poly-Si thick films via thermal CVD at different deposition temperatures. The Raman spectra for poly-Si thick films grown by a solid-phase crystallization (SPC) process and for crystalline Si wafer are also included for comparison. Table 1 summarizes the experimental results obtained from Raman spectra for the poly-Si thick films. It was reported that the spectra can be fitted by one Lorentzian component and two Gaussian components in Raman spectra at around 520, 480 and 500 cm^{-1}, respectively, corresponding to

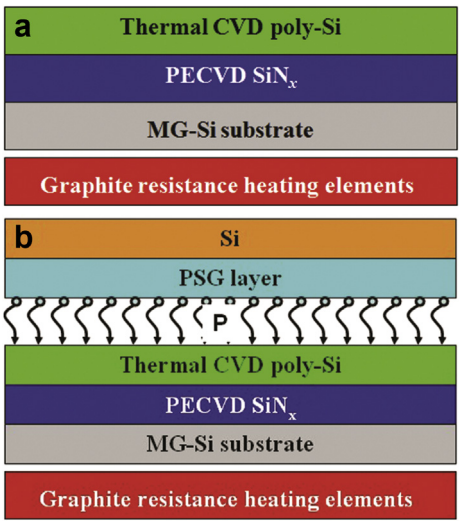

Fig. 1 Schematic diagram for: (a) depositing poly-Si thick films, (b) obtaining P-doped poly-Si thick films on SiN_x-coated MG-Si wafers.

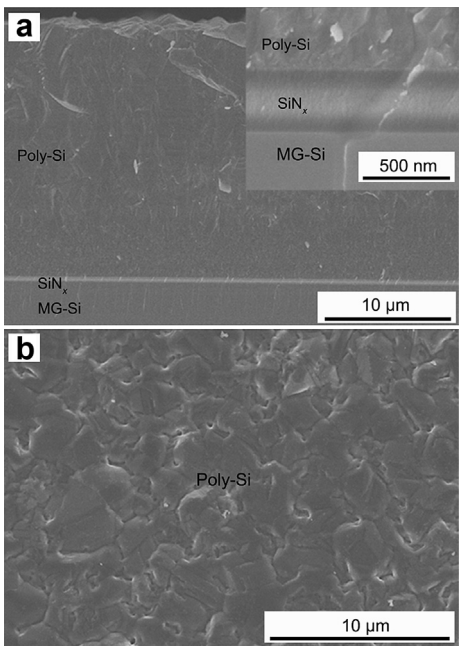

Fig. 2 Cross-section (a) and top-view (b) SEM images of the poly-Si thick films deposited on SiN_x-coated MG-Si wafers. Inset in (a) shows the enlarged cross-section image.