Improvement of Reflectivity in Silicon Wafers through the Generation of Porous Silicon and its Chemical Attack with Potassium Hydroxide

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Meeting-report

Improvement of Reflectivity in Silicon Wafers through the Generation of Porous Silicon and its Chemical Attack with Potassium Hydroxide

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Crystalline silicon (C-Si) reflects approximately 30% of incident sunlight [1]. Numerous studies have been carried out to improve this performance, reducing the reflectance in C-Si-based solar cells [2,3]. A common strategy to achieve this is using anti-reflective coatings (ARC) [4]. Among the most widely used ARCs for silicon solar cells is silicon nitride, which is reported to reduce the integrated reflection to around 10% [4]. Macroporous silicon (MPS) is a material that can be obtained by electrochemical anodization from monocrystalline silicon surfaces [5,6]. By carefully selecting the manufacturing parameters, it is possible to obtain porous structures consisting of cylindrical pores with a high aspect ratio. In this way, it is feasible to manufacture pores of approximately one micrometer in diameter. The presence of empty spaces in a silicon matrix reduces the reflectance since this new material modifies its optical properties by combining the refractive indices of silicon and air [7]. The generation of inverted pyramids from the marking of silicon by photolithography and, subsequently, an attack with alkaline solutions such as KOH or NaOH also minimize the reflectance due to multiple internal reflections in the inverted pyramid of the incident light beam [8]. In this work, we optimized the thickness of the porous layer to reduce the reflectance and, subsequently, a chemical attack with KOH; both techniques left a reflectance at 365 nm of 17% compared to crystalline silicon of 72%.

The MPS layers were prepared by electrochemical anodization of p-type boron-doped crystalline silicon wafers (with a resistivity of 30-40 Ωcm and (100) orientation) in a solution composed of 50% hydrofluoric acid and 99.8% dimethylformamide in ratio 1:9 (v/v). The galvanostatic process was carried out for 20 minutes with a 12 mA/cm² current density under dark conditions. A Teflon® anodizing cell was used with a platinum electrode as the cathode and the silicon wafer as the anode. After the electrochemical attack, the samples were rinsed with ethanol and dried under a flow of N_2 gas. Then, the pore surfaces were chemically attacked by immersing the samples in potassium hydroxide with a concentration of 1M dissolved in water for different periods. They were then rinsed with deionized water and dried again with N_2 gas. This treatment generates inverted pyramids at the tips of the pores, contributing to a decrease in reflectance. The morphology of the MPS film was examined by Scanning Electron Microscopy (SEM) with a JEOL JSM-35C SEM, using electron energies of 20 kV, and images were analyzed with the free UTHSCSA ImageTool Version 3.0 software.

Top view and cross-sectional SEM images of MPS films are presented in Figure 1. Figures 1(a) and 1(b) correspond to freshly anodized MPS samples. In Figure 1(a), ovoid-looking pores of different sizes are observed. Using an image analyzer, the average pore diameter was determined to be approximately 1 µm. In Figure 1(b), it can be seen that the growth of the pores is perpendicular to the substrate. The shape of the pores is almost cylindrical, with an average length of 20 µm. It is observed that the pores obtained do not present branches or connections between them, unlike what happens with mesoporous silicon [9]. Another characteristic of the pore walls is their rough appearance along the pore's length, and the pores' thickness is not homogeneous, especially at the tips and tails. Figures 1c) and 1d) correspond to samples etched with potassium hydroxide after anodizing. Ovoid-looking pores turn into rectangular-looking pores after the attack. This rectangular appearance is due to the silicon's crystallographic (100) orientation. It is possible to observe the formation of inverted pyramids in some shallower pores (pores of less dark color). In Figure 1d), the inverted pyramids are more notable at the tips of the pores, where a well-defined triangle-shaped termination can be seen, which is consistent with what was observed in the superficial part of the pores. The pore walls show less roughness due to the KOH attack, eliminating surface imperfections. The inverted pyramids and the increase in pore diameters generate structural changes that are reflected in the decrease in reflectance. The KOH attack eliminates imperfections, which causes the pore diameter to be more homogeneous along its length.

Figure 2 presents the reflectance spectra of samples etched by electrochemical method and subsequent chemical etching with KOH in the wavelength range of 300 to 800 nm. The spectra of the polished c-Si before etching are shown for comparison purposes. It can be observed that the optical reflectance spectra of c-Si are reduced by 32% at the wavelength of 365 nm after electrochemical etching. Immersing the MPS in a KOH solution for one minute decreases the reflectance by 36% concerning the initial reflectance. It is observed that the reflectance of silicon continues to decrease as the MPS attack time increases.

From the SEM images, it was found that the pores have a large aspect ratio with cylindrical pores; these grow during the anodizing of the silicon perpendicular to the substrate with an ovoid pore shape and with a diameter of 1 µm and 20 µm long without branches. After the chemical attack with KOH, these ovoids generate rectangular-looking pores, and the pores' tips generate inverted pyramids responsible for the decrease in reflectance due to multiple refractions of the incident beam that interacts with the surface. The etching with KOH generates pores with fewer imperfections in the walls, and their diameter is more constant along the pore. These structural changes decrease reflectance; crystalline silicon has a reflectance of 72%; after electrochemical etching, the reflectance decreases to 39%, and after 4 minutes of KOH, the reflectance is 17%.

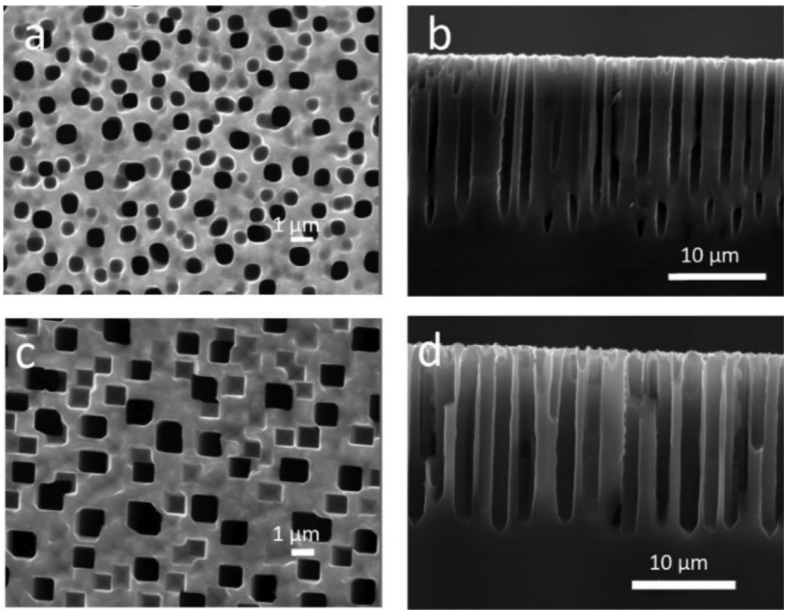

Fig. 1. SEM images of a) top view of MPS before KOH etching, b) cross-sectional view of an MPS layer before KOH etching, c) top view of MPS after KOH etching, d) Cross-sectional view of an MPS layer after KOH etching.

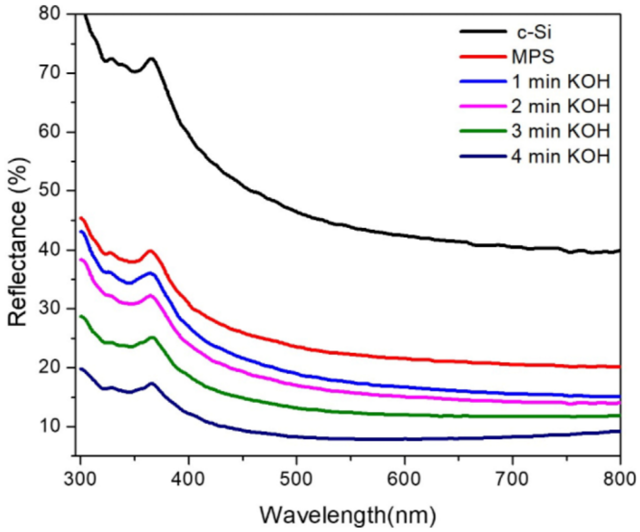

Fig. 2. Reflectance spectra of different silicon substrates

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