Change in optical properties by texturing Si compounds by F_2 and NO_x gases

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1. Introduction

Reducing light reflection from the surface of photovoltaic cells made of silicon nitride films deposited on the textured single or multi crystalline Si plays a key role to improve the cell efficiency. Recently, chemical dry etching using ClF_3 have been intensively studied to texture single and/or multi crystalline Si [1, 2]. In order to reduce the process cost and the process chamber corrosion induced by Cl, we have been investigating the nanoscale Si surface texturing using etch species generated by the reaction of $F_2 + NO_x$ (X=1, 2) → $F + FNO_x$ [3, 4]. In this study, we evaluated the change in optical properties of various Si compounds by modulating the NO/F_2 ratio that would modify the nanoscale surface texturing by controlling the adsorption of F_2, NO_x, F, and FNO_x on the Si surface. The chemical bonding structures, responsible to pattern the Si surface, were predicted by the density functional theory (DFT) using CAM B3LYP 6-311 G+(d,p) in *Gaussian 09*.

2. Experimental and Calculation

Non-doped Si(100) 10 x 10 mm^2 samples were washed in acetone, ethanol, DI water and diluted hydrofluoric acid solutions for 5 min each followed by immersing in DI water for 1 s to terminate the surface with hydrogen bond. This sample was placed in the Pyrex tube and the total of 107-109 sccm of Ar/5-10%F_2 + NO_x were introduced to the etching apparatus by varying the flow rate ratio of NO_x/F_2 and the substrate heating temperature from 15 to 300°C. The pressure was maintained at 600 Pa during the etching time of 5-60 min. The surface chemical bonding structure was calculated by DFT, measured by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy. The surface morphology (roughness) was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Reflectance measurements were performed using HR4000 spectrometer (Ocean Optics) that could measure 300-1100 nm while the average reflectance was measured from 500-850 nm.

3. Results and Discussion

Figure 1 shows the SEM images of the textured Si surface, the root-mean-square (rms) roughness obtained from 10 μm line profile in the 100 μm^2 scan area, and the reflectance. The reflectance was reduced by 2/3 to 1/2 when the surface have different sizes of etch pits generated by the chemical adsorption of F_2, NO_x, F, and FNO_x. Based on the reaction model generated by the DFT calculation, F_2, F, and FNO promoted the etching while NO_x and FNO_x acted as etching inhibitor by capping the dangling bond. NO_x rich surface generated by the NO_x/F_2 ratio of ~ 2.2 showed the lowest reflectance due to the presence of NO_x rich bond that would act as a nanoscale etch mask to generate the 30-50 nm nanoscale etch pits and the width of the etch pit of ~ 100 nm. The size of the etch pit is close to the width of the previously reported Ag island to improve the photovoltaic efficiency by increasing the scattering efficiency [5].

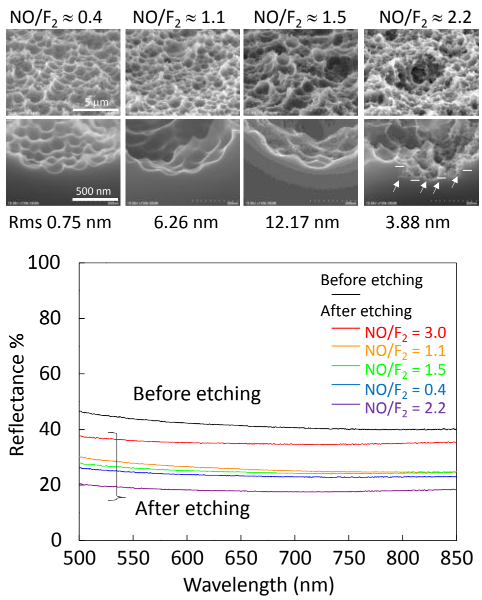

Fig. 1. The SEM images, surface roughness, and the reflectance from the Si surface etched in F_2 and NO_x gases.

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