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Short Communication

New method for boron removal from silicon by electron beam injection

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ABSTRACT

A new method for boron removal from silicon using electron beam injection (EBI) is proposed. After thermal oxidation on monocrystalline silicon (100) wafer at 1000 °C for 1 h, EBI was used to induce thermal and negative charging effects to enhance boron diffusion in the oxide film and the silicon substrate. This facilitates boron removal from the silicon substrate. The boron concentration in samples was measured by secondary ion mass spectrometry. The results show that EBI reduced the boron concentration in the silicon substrate by 4.83%.

1. Introduction

Metallurgy is believed to be an effective and energy-saving approach for producing solar-grade silicon. The method involves removing impurities from metallurgical-grade silicon, including metals such as iron, calcium, and aluminum, and nonmetals such as phosphorus and boron. These impurities have a negative effect on the electrical properties and efficiency of solar cells. Metals can be removed effectively by directional solidification [1,2]. Phosphorus can be removed by electron beam melting [3,4].

Boron has stable physical and chemical properties in silicon, so it is not easy to remove. Researchers have studied this problem for many years. The JFE company in Japan used a plasma beam to ionize H_2O and generate O^- and OH^- to react with boron to facilitate its escape from silicon [5]. Other methods include slagging [6] and Si–Al alloy formation [7]. However, there has been no research on the use of electron beam injection (EBI) to remove boron from silicon.

Here we propose EBI as a new method for boron removal from silicon. We measured boron concentrations in silicon and SiO_2 film before and after EBI. EBI reduces the boron concentration since thermal oxidation causes boron redistribution from the silicon to the oxide film [8]. Boron can be electropositive in oxide films since it can form O–B–O bonds when it diffuses in amorphous SiO_2 [9]. The SiO_2 film can be negatively charged during EBI due to the negative charging effect [10]. The negatively charged oxide film can induce diffusion of electropositive boron from inside the substrate to the surface. The thermal effect of the electron beam can also enhance boron diffusion. Thus, EBI facilitates boron removal from silicon.

2. Experimental

The samples used were monocrystalline silicon (100) wafers of 450 μm in thickness. The wafers were polished on one side and had a high boron doping concentration. They were cut into squares with an area of 1 cm^2. Each sample was cleaned ultrasonically in deionized water for 30 min and then dried in an oven.

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SiO_2 films were generated by thermal oxidation of the polished side in a tubular resistance furnace at 1000 °C for 1 h under a continuous flow of oxygen gas. A silicon wafer with a homogeneous oxide film was then selected for EBI. The procedure was carried out using a 30-keV electron beam at 20 mA for 30 min in an electron beam melting furnace with a vacuum $<5\times10^{-2}$ Pa.

Field-emission scanning electron microscopy (FE-SEM) was used to investigate the surface morphology of the samples. The structure of the oxide film was characterized by X-ray diffraction (XRD). An ellipsometer was used to measure the thickness of the oxide film before and after EBI process. Boron concentrations were measured by secondary ion mass spectrometry (SIMS).

3. Results and discussion

Fig. 1a–c shows SEM images of the surface morphology. The surface of the SiO_2 film obtained by thermal oxidation has a much more homogeneous structure than for the original silicon surface. However, after EBI the oxide film has many cracks. This indicates that electron beam bombardment causes cracks on the surface of the oxide film.

XRD patterns for the samples are shown in Fig. 1e. The only peak for the original silicon wafer (69.235°) corresponds to the silicon (400) plane, which is in the same crystal plane family as (100). This confirms that the original silicon wafer was monocrystalline. XRD patterns for the oxide film before and after EBI have no peak, indicating that the SiO_2 films are both amorphous and the structure is not affected by EBI.

The thickness and color of the oxide film before and after EBI are shown in Table 1. The color did not change, while the thickness decreased to 7.829 nm after EBI. This is probably because electron beam bombardment removes some surface SiO_2 under the vacuum environment.

Fig. 2 shows the boron concentration profile according to SIMS. The boron concentration in the original silicon wafer is almost uniform since boron is doped into the silicon during crystal growth.

The boron concentration profile after thermal oxidation is in general agreement with the theoretical curve for impurity uptake by oxide [8]. The surface boron concentration is lower than in the original silicon because of volume expansion when silicon forms SiO_2. The boron concentration is higher on the SiO_2 side than on the silicon side because of the segregation of boron from silicon to oxide [8].

The Si (raw silicon counts) curve in Fig. 2 represents the silicon ion intensity during SIMS. This curve indicates the transition from SiO_2 film to the silicon substrate since the rate of Si ionization is much higher in SiO_2 than in silicon. The curve breaks at ~98 nm and then decreases rapidly to a stable value at ~149 nm, indicating a transition between SiO_2 and silicon in this area rather than a clear interface. We call this area the transition region. The boron concentration gradually changes in the transition region, which differs from the theoretical curve.

The boron concentration in the silicon substrate after thermal oxidation was integrated over depth from 155 to

Table 1
Results for oxide film thickness and color before and after EBI.

	Thickness (nm)	Color
Before EBI	134.785	Light blue
After EBI	126.956	Light blue

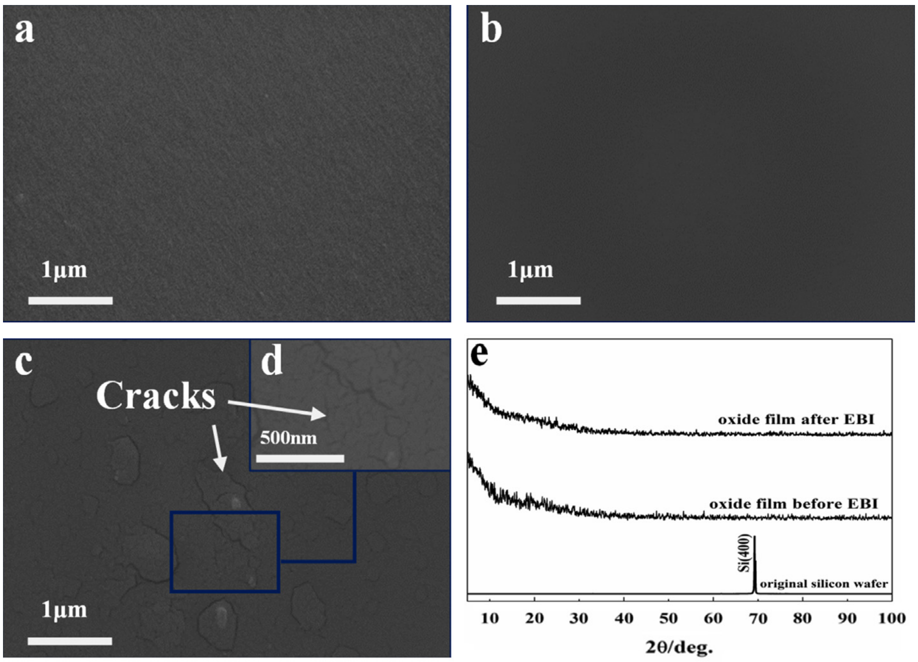

Fig. 1. SEM images and XRD patterns for the samples. (a) Surface of the original silicon wafer. (b) Surface of the SiO_2 film before EBI. (c) Surface of the SiO_2 film after EBI. (d) Higher magnification of the SiO_2 film after EBI. (e) XRD patterns for the original silicon wafer and the oxide films before and after EBI.