Materials Science-Poland, 35(1), 2017, pp. 14-17
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.1515/msp-2017-0027

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Effect of electron beam injection on boron redistribution in silicon and oxide layer

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The behavior of boron redistribution in silicon with and without oxide layer after electron beam injection (EBI) was investigated. Special defect shapes were generated on the surface of bare and oxidized silicon wafers. Secondary ion mass spectrometer was used to measure the boron profile. The results showed that after long EBI time, boron tended to be induced from both sides of the transition region between the oxide layer and silicon. For the sample without oxide layer after EBI, boron tended to diffuse towards the surface and its concentration obviously reduced inside the silicon. The results of the study show the potential use of the process in removing boron impurity in silicon.

Keywords: *electron beam injection; silicon; solar energy materials; boron; oxidation*

1. Introduction

The removal of impurities in silicon is the core technology in solar-grade silicon industry. Metallurgical method has been proven to be an effective and energy-saving way to produce solar-grade silicon. In this method, metal impurities are removed by directional solidification due to small segregation coefficients of these metal elements in silicon [1, 2]. Nonmetal impurities, such as phosphorus, can be removed by electron beam melting [3, 4].

Boron impurity in silicon is difficult to remove because of its stable physical and chemical properties. Traditional methods, such as gas blowing, plasma beaming, slagging and Si–Al alloy formation, have been applied [5–8]. Some other methods concerning boron gathering and redistribution in silicon and oxide layer have also been proposed. Abadli et al. [9] have investigated the complex behavior of boron redistribution process in silicon thin bi-layer interface and developed its redistribution model. The influence of F elements on boron redistribution in Si and SiO_2 has also been studied [10]. Grove et al. [11] found that boron can redistribute from silicon to oxide film by thermal oxidation. Boron can be electropositive in oxide layer and forms O–B–O bond when it diffuses in amorphous SiO_2 [12]. Negative charging effect can cause the SiO_2 layer to be negatively charged during electron beam injection (EBI). Based on these discoveries, electron beam was used to inject electrons into the oxide layer to make it charge negatively, and then induce electropositive boron from inside to the surface. Through this process, boron can be removed from silicon [14].

In this study, various EBI times were explored to investigate the effect of EBI time on boron redistribution in silicon and oxide layer, and also determine boron diffusion behavior in oxide layer and silicon. A bare silicon wafer was subjected to the EBI process to evaluate the behavior of boron redistribution in silicon without oxide layer.

2. Experimental

The used (1 0 0) monocrystalline silicon wafer with the thickness of 420 µm was highly doped

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with boron and then polished on one side. The samples were cut into small squares with an area of 1cm^2. The samples were soaked in deionized water, cleaned in an ultrasonic cleaner and dried in an oven.

The SiO_2 layer was obtained on the polished side through thermal oxidation. The experiment was performed in a tubular resistance furnace at 1000 °C for 1 h with continuous oxygen gas flow. Then, the samples with homogenous oxide layer were subjected to EBI in an electron beam melting furnace which operated at a vacuum pressure lower than 5×10^{-2} Pa and a 30 keV electron beam. One sample with oxide layer was subjected to EBI at 20 mA for 1 h and the other sample for 2 h. The wafer without oxide layer was subjected to EBI at 20 mA for 1 h. The structure of the oxide layer was characterized by an PANalytical Empyrean D8 Advance X-ray diffractometer (XRD) which has a frequency of 50 Hz to 60 Hz and maximum power of 2.2 kW. A SUPARR 55 scanning electron microscope (SEM) with a 15 kV electron gun and 0.8 nm resolution was used to observe the surface morphology of the samples before and after EBI. The boron concentration profile was measured with a secondary ion mass spectrometer (SIMS) within the atoms detection limits of $>10^{10}$/cm^3 to 10^{16}/cm^3.

3. Results and discussion

SEM micrographs of the oxide layer surfaces after EBI are shown in Fig. 1. Different defect shapes have been generated on the surface. As shown in Fig. 1b, regular square defects are distributed sporadically, and each defect has a circular hole at the center. Irregular defects, such as tadpole-shaped defects, are also observed, as shown in Fig. 1c. These special defects are caused by the bombardment of the electron beam. The XRD patterns of the samples are shown in Fig. 1d. The patterns of the oxide layers before and after EBI do not show any peaks, indicating that the SiO_2 layers are amorphous, and the structure type has not changed by EBI.

The SIMS profile of boron concentration is shown in Fig. 2. The “Si (raw silicon counts)” curve

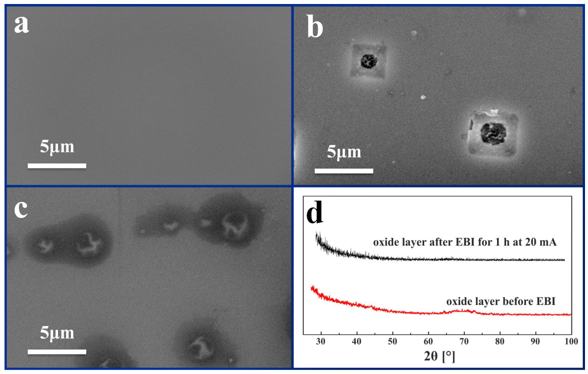

Fig. 1. SEM images and XRD patterns of the samples: (a) surface of the oxide layer before EBI; (b) and (c) surfaces of the SiO_2 film after EBI; (d) XRD patterns of the oxide layers before and after EBI.

represents the silicon ion intensity. It indicates the transition region from the oxide layer to the silicon substrate because the ionization rate of silicon atoms in SiO_2 is much higher than in silicon. The curve breaks at 81 nm and then decreases rapidly, finally reaching a stable value at 115 nm. The boron concentration also shows a gradual transition in this region. The boron profile after thermal oxidation is consistent with other reports in the literature [15, 16]. Segregation occurs during thermal oxidation, and boron migrates into the oxide layer and its concentration decreases with depth.

After EBI, the surface boron concentration decreases, as some of the boron atoms separate from the oxide layer to vacuum environment, when electron beam is bombarding the surface. The surface boron concentration decreases further with longer EBI time. In the oxide layer, boron concentration increases as EBI time increases. With longer EBI time, the temperature of the sample reaches equilibrium, hence, the enhanced negative charging effect may be the main reason for the increase of boron concentration in the oxide layer.

In the transition region, boron piles up after EBI. An obvious concentration peak is observed in this region after 2 h EBI, indicating that the transition region as well as the interface of oxide layer and silicon substrate induces more boron from both sides with the increased EBI time. Given that boron and oxygen atoms form O–B–O bonds, when they diffuse into the oxide layer, the special boron concentration in the transition region indicates the presence of numerous O–B–O bonds existing in this region. After prolonged EBI process, this region becomes more negatively charged and continuously induces boron from both sides. This region enhances boron redistribution. However, it is also a barrier for boron to diffuse from silicon to the oxide layer. For the silicon substrate, boron concentration is nearly the same before and after EBI, indicating that longer EBI time has a limited effect on silicon substrate with an oxide layer.

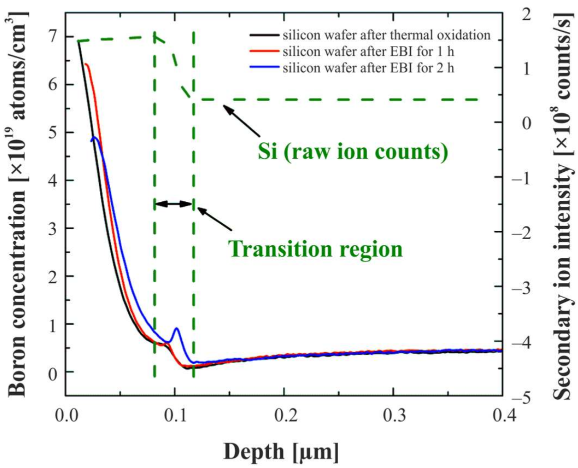

Fig. 2. SIMS profile of boron concentration.

The surface morphology of silicon wafer without oxide layer after EBI is shown in Fig. 3. The electron beam bombardment generated many parallel and crossed traces which are distributed on the sample. Defects are also distributed among the traces, as shown in Fig. 3d. This special morphology can be helpful for boron diffusion because impurities tend to pile up toward defects.

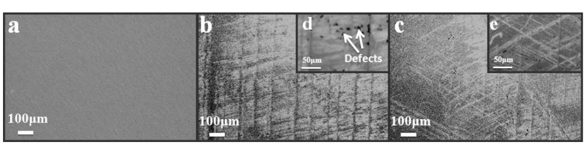

Fig. 3. SEM images of silicon wafer surface: (a) surface of the silicon wafer before EBI; (b, d) and (c, e) surfaces of the silicon wafer after EBI for 1 h.

The boron profile in silicon wafer without oxide layer after EBI for 1 h is illustrated in Fig. 4.

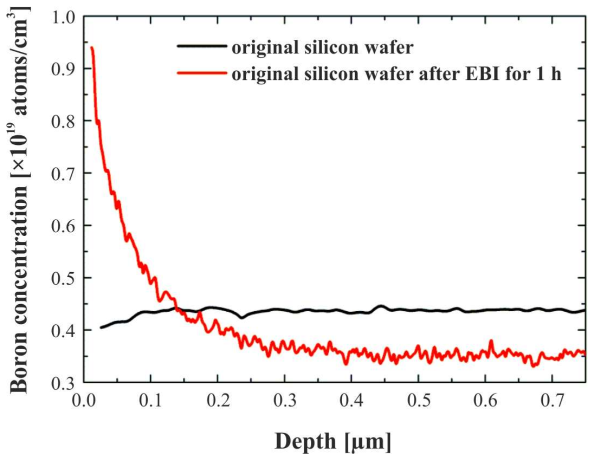

Fig. 4. SIMS profile of silicon wafer without oxide layer.

The surface boron concentration after EBI is extremely high, and boron concentration inside the silicon is lower than in the original wafer without EBI. This phenomenon indicates that EBI can induce boron impurities in silicon. EBI increases the temperature of the sample by the thermal effect of electron beam. Diffusivity increases, resulting in linear relationship between the reciprocal of temperature and the logarithm of boron diffusivity in silicon [17]. Thus, EBI enhances the ability of boron diffusion. Because the sample thickness is only 420 μm, so the sample temperature has been assumed to be uniform during the EBI. Therefore, to account for the impetus resource of boron diffusion from inside towards the surface, a second effect, which is the charging effect of EBI, has been proposed. Since electron beam contains many electrons, an electric field is formed when it bombards the sample. The intensity of this electric field around the surface is obviously higher than that inside the silicon. Consequently, the electrons which are injected into the sample can induce boron atoms, and the higher electric field intensity on the surface provides the impetus for boron diffusion from inside to the surface. Based on Baierle study [18], boron impurity in silicon is electropositive, and the electronegative SiO_2 film can absorb boron atoms. In this study, the formed electric field is also electronegative, so it can induce boron atoms during the injection process. The defects on the surface, which are shown in Fig. 3b, can be helpful for this process because boron tends to pile up toward the defects. Electron beam bombardment can separate some of the boron atoms from the surface to vacuum environment continuously, further promoting boron to move towards the surface. Thus, boron continues to diffuse from inside toward the surface.The EBI process needs lower energy than electron beam melting because it only uses electron beam to irradiate silicon. Therefore, this process can be a promising way to remove boron impurity from silicon, and can enhance the application of electron beam in silicon refining.

4. Conclusions

The behavior of boron redistribution in silicon with and without oxide layer during EBI has been investigated. Longer EBI time has limited effect on boron impurity concentration in silicon substrate with oxide layer. However, after EBI, the transition region as well as the interface of oxide layer and silicon substrate tend to induce boron from both sides. This effect can be enhanced with longer EBI time. After EBI, boron in silicon without oxide layer diffuses toward the surface, and the boron concentration inside silicon is reduced. The electric field, which is formed during EBI, is proposed to be the main reason for this behavior. This process can be developed as a new way to remove boron from silicon.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 51074032 and U1137601), the Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 20130041110004).

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Received 2016-02-29
Accepted 2017-01-15