Removal of Oxides and Surface Texturization of Crystalline Si Wafer by Ion Beam Etching

Yan LI1,* and Yoshimine KATO2

1Department of Automotive Science, Graduate School of Integrated Frontier Science, Kyushu University, Fukuoka City 819-0382, Japan
2Faculty of Engineering, Kyushu University, Fukuoka City 819-0382, Japan
*Corresponding author

Keywords: Ion beam etching, Si oxides, Water contact angle, Surface texturing.

Abstract. Surface oxides of crystalline Si wafer (c-Si) has been etched by argon (Ar) ion beam (IB) bombarding. The contact angles of water droplet (WCA) on the c-Si wafer, before and after IB etching, have been measured. It’s been observed that the c-Si wafer surfaces turn to hydrophobic after IB etching. This may be due to a surface texturization by ions bombarding. The cleanliness of wafer surfaces has been evaluated as well. It is speculated that IB etching may be an alternative to hydrofluoric acid (HF) in terms of Si oxides removal and be advantageous because of its non-chemical hazardousness. The IB bombarding may also be applied to the fabrication of c-Si solar cells, for the purpose of forming the anti-reflection layer via texturization.

Introduction

The surface of c-Si wafers is covered by a thin native oxides layer which is dense and firm. This layer could prevent the further oxidation of inner wafer. Usually, the Si oxides layer makes the wafer to be hydrophilic, due to the Si-OH groups linked [1]. In the semiconductor industry, the removal of this Si oxides layer is usually done through the wet etching process. HF is the chemical most commonly used to clean the Si oxides. It has been confirmed that after HF etching, Si wafer surfaces are terminated by a hydrogen monolayer. This layer may be the reason that etched Si wafers are hydrophobic [2]. However, HF is not always desired, drawbacks include that it is volatile, erosive and highly hazardous to human body. As a result, protections are much necessary. IB milling has been introduced to the semiconductor industry for decades [3]. Enlighted by the IB milling and in realization of the unfavorableness of HF, IB etching has been adopted. Here in this work, it is introduced that IB could effectively remove the surface oxides, native or thermally grown, of c-Si wafers. And interestingly, it is noticed that surface texturing has been achieved simultaneously after the deep etching. The IB bombarding thus could be considered as an alternative to HF etching. The texturization property of IB etching to c-Si solar cells may also indicate that it can be applied to the solar cell industry.

Experimental

N-type (antimony doped) (100)-oriented c-Si wafer (resistivity of 13-16 mΩcm) was cut into pieces that have a 1 x 1 cm² nominal dimension. Then they were cleaned by ultra-sonication in ethanol for 5 min. Before & after IB etching, one droplet of de-ionized water (about 0.02 ml) was dropped on each c-Si wafer. Cross-section view of water droplets were recorded with a digital camera and WCAs were then measured by the classical θ/2 method, if one assumes that the water droplet is part of a sphere [4]. IB etching was performed by using an ion beam generator. Inside the main chamber, flow rate was regulated by a gas flow controller. For all experiments, a total flow rate at 15 sccm was adopted. The source gas was Ar (6N purity) or a mixture of Ar+10% H₂ (in terms of H₂ flow rate). Beam current & voltage, acceleration current & voltage and discharge current & voltage were monitored and controlled by an ion gun/beam source power supply (Ion Tech Inc. MPS-5001). For wafer pieces to be etched, duration of IB bombardment was set at 90 min.
In order to estimate the effectiveness, Fourier-transformed infrared (FT-IR) spectrometer (Perkin Elmer Spectrum Two) has been employed to analyze the oxides peaks. For all measurements, a total accumulation of 16 times was performed. Some c-Si wafers were annealed at 900, 1000 and 1100 °C for 30 min in the open air to grow thermal oxides. After annealing, parts of annealed wafers were HF etched (3 wt.%) for 1 min, while the others were IB etched for 90 min using the setting mentioned above. IR spectra from HF- or IB-etched wafers were then collected for the comparison of cleanliness.

Silver electrodes were deposited on c-Si wafer after annealing. I/V characteristics of annealed samples were measured by a power device analyzer/curve tracer (Agilent Technologies B1505A). Surfaces morphology of c-Si wafer were observed by a SEM (Hitachi SU-8000) operated at an acceleration voltage & current of 1.0 kV and 10 μA, respectively.

Results & Discussion

FT-IR

As shown in Fig. 1 (a), the wafer samples annealed at 900 °C (in the open air) for 30 min exhibits an adsorption peak at around 1100 to 1200 cm⁻¹, which is due to the Si-O asymmetrical stretching mode (Si-O AS). Similar results were observed for wafers annealed at 1000 or 1100 °C, as well. The small peak around 450 cm⁻¹ for Si wafers annealed at 1000 (Fig. 1 (b)) and 1100 °C (Fig 1. (c)) was attributed to the Si-O rocking mode (Si-O R) [5]. IR spectra indicates that Si thermal oxides were grown on the surfaces of wafer after annealing in the open air. Those oxides peaks disappeared either after a HF- for 1 min or an IB-etching for 90 min. Therefore, it is confirmed that thermal oxides only formed at the surfaces of wafers and were completely removed by either HF etching or IB bombardment. The results also prove that IB bombardment may be used as an alternative method for oxides cleaning, and be advantageous to HF, because of its less hazardousness.
Figure 1. IR spectra of c-Si wafers annealed at (a) 900, (b) 1000 and (c) 1100 °C, respectively. IR spectra of each annealed (under respective temperatures) samples after either IB etching or HF etching are plotted as well.

**I/V Sweep**

Current-voltage characteristics of wafers, annealed in the open air and IB etched, were measured to evaluate the effectiveness of IB cleaning. The I/V curves are plotted in Fig. 2. As an insulator, the thermally grown Si oxides could greatly increase the resistance of c-Si wafer. For the annealed Si wafer, current is in pico-Ampere scale (roughly 30 pA at 0.5 V, corresponding to a resistance around 16.7 GΩ). After a 90-min IB etching, its current drastically increases to milli-Ampere scale (around 1 mA at 0.5 V, equal to a resistance of 500 Ω).
Figure 2. I/V characteristics of wafer (annealed at 900 °C in the open air) before and after a 90min-IB cleaning. The order of magnitude has increased almost 10^9, from pA scale to mA scale.

By combining the results from FT-IR and I/V sweep, one can conclude that IB etching could effectively remove the surface oxides of c-Si wafer, even if the oxides layer is thermally grown and thus relatively thick. It is therefore possible to estimate the etching rate of surface Si oxides by IB etching as well. If one assumes that the thermal oxides layer is a few hundred nanometers thick, then the calculation indicates that the etching rate would be 1-3 nm/min, allowing for precise control of the oxides thickness.

WCAs & SEM

Figure 3 (ion source gas is Ar) & Fig. 4 (source gas is Ar+10% H\textsubscript{2}) show the WCAs of n-type c-Si wafers (a) before & (b) after a 90-min IB etching. With native oxides covering c-Si wafer, WCAs, roughly at 37 °, clearly are much smaller than those after etching. This indicates that native oxides make the surface of c-Si wafer more hydrophilic, when compared to the IB-etched Si surfaces. As depicted in Fig. 3 (b) and Fig. 4 (b), with WCAs at roughly 90 ° and 78 °, the Si wafer surfaces get more hydrophobic. It has been already found that HF etched c-Si wafer could become hydrophobic which is due to the hydrogen (H) termination, WCAs are around 78 ° in our case while photos are not shown here. But usually this kind of H-termination is not very stable and with time elapsing, the cleaned Si surface will be oxidized again so the WCA may get smaller [6]. However, for the IB etched Si wafer, it is observed that WCAs remain almost the same even after 2 years.

Figure 3. WCA of c-Si wafer (a) before (WCA ~ 37 °) and (b) after a 90min-IB etching (Ar as source gas, WCA ~ 90 °).
SEM photos in Fig. 5 may uncover the reason that IB (ion source gas is Ar) cleaned c-Si wafer is hydrophobic. The Si wafer surface is highly rough, with a “pyramid-like” pattern. When de-ionized water was dropped on top of the wafer, surface tension of this droplet, together with the rough wafer top layer, makes it difficult to spread and tend to remain the shape of a semi-sphere. Consequently, macroscopically a hydrophobic property of c-Si wafer to water droplet could be observed. Similarly, in Fig. 6, the IB etched (source gas is Ar+10% H$_2$) wafers have a rough surface as well. Its pattern is “stripe-like”. The smaller WCAs (~78 °) compared to that of wafer (~90 °) shown in Fig. 5 may be attributed to insufficient etching. Hydrogen ions are much lighter than Argon ions, thus carrying much less energy. The physical collision to Si wafer surface should thus be less powerful, leading to a relatively smaller roughness. So as a result, WCAs are smaller, namely ~78 ° compared to ~90 °. Nevertheless, a detailed research towards this phenomenon is necessary to verify the abovementioned discussion.

Figure 4. WCA of c-Si wafer (a) before (WCA ~ 38 °) and (b) after a 90min-IB etching (mixture of Ar+10% H$_2$ as source gas, WCA ~ 78 °).

Figure 5. SEM images of c-Si wafer surface after a 90min-IB etching (Ar as source gas), magnified by (a) 150k and (b) 20k, respectively. A “pyramid-like” textured surface could be clearly observed.
Conclusion

In this work, surface oxides of c-Si wafer have been successfully removed by Ar+ IB bombardment. FT-IR spectra of c-Si wafer after annealing in the open air & after IB etching have been collected. The results indicate that IB etching is highly effective for the removal of Si oxides and is comparable to HF. The WCA reached a maximum after a 90-min IB bombardment (source gas is Ar). SEM images reveal the surface morphology of IB etched wafers. The textured surfaces may be the reason that causes wafers to be hydrophobic. This work shows that IB etching has the potential to be applied to solar cell industry as well.

Acknowledgement

This work was supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Number JP16K13720.

References

[1] X.M. Yang, Z.W. Zhong, E.M. Diallo, Z.H. Wang and W.S. Yue, Silicon wafer wettability and aging behaviors: Impact on gold thin-film morphology, Mater. Sci. Semicond. Process., 26 (2014) 25-32.

[2] Y. Sato and M. Maeda, Study of HF-Treated Heavily-Doped Si Surface Using Contact Angle Measurements, Jpn. J. Appl. Phys., 33 (1994) 6508-6513.

[3] L. Mader and J. Hoepfner, Ion Beam Etching of Silicon Dioxide on Silicon, J. Electrochem. Soc.: Solid-State Science and Technology, 123 (1976) 1893-1898.

[4] Y. Yuan and T.R. Lee, Chapter 1: Contact Angle and Wetting Properties, in G. Bracco and B. Holst (Eds.), Surface Science Techniques, Springer-Verlag, Berlin Heidelberg, 2013, pp. 3-34.

[5] C.T. Kirk, Quantitative analysis of the effect of disorder-induced mode coupling on infrared absorption in silica, Phys. Rev. B, 38 (1988) 1255-1273.

[6] S.B. Habib, E. Gonzalez II and R.F. Hicks, Atmospheric oxygen plasma activation of silicon (100) surfaces, J. Vac. Sci. Technol. A, 28 (2010).