OPTIMIZING STABILITY OF WET CHEMISTRY OXIDE PASSIVATION OF Si (111) AND Si (100)

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ABSTRACT

Numerous parameters are regulated in the wet chemical oxidation process for TOPCon/POLO solar cell technology to improve silicon oxide passivation (SiO_2). Understanding the electronic properties, particularly the lifetime of the carriers and their thickness, requires knowledge of the properties of the surface of crystalline silicon (c-Si), which is subjected to native oxide etching, followed by wet chemical oxidation, such as nitric acid or hot water oxidation and various hydrogenation methods. The results of these processes are tracked with lifetime measurement equipment, and spectral ellipsometry is used to measure the thickness of the oxide layer by using the single-sided polished wafers with surface orientation (1 1 1). In addition to the actual values, their time stability is also tracked. Before the hydrogenation step was introduced, the wafers' lifetime was approximately 0.001 ms, which is less than the bulk lifetime; with the hydrogenation, the lifetime increased by more than an order of magnitude for a relatively long time with no difference between (1 1 1) and (1 0 0) wafers indicating that hydrogenation of the Si/SiO_2 interface is performed.

Keywords: solar cells, silicon, surface passivation, TOPCon, wet chemical oxidation, spectral ellipsometry, carrier lifetime.

INTRODUCTION

Silicon is the finest material for creating a solar cell for two key technological reasons [1]. Primarily, it is the second most abundant material, and secondly, it has a permanent oxide layer that provides excellent electrical insulation. Furthermore, the low defect density at the Si/SiO_2 interface makes it ideal for electrical applications. To produce the desired SiO_2 layer, various oxidation methods such as thermal oxidation, wet chemical oxidation and plasma-enhanced oxidation are commonly used. Each approach has its benefits, and the best one is chosen depending on the particular needs of the semiconductor fabrication process, e.g. thermal oxidation is at least as good as wet chemical oxidation.

The wet chemical oxidation can easily be implemented in wet bench processing to avoid high thermal bonding.

The wet chemical oxidation of silicon has a long history that began in the 1950's with the development of semiconductor technology. Researchers at that time were investigating several techniques for growing oxide layers on silicon substrates. One of the early methods required heating silicon wafers to temperatures above 800°C while exposing them to a combination of water vapour (H_2O) and oxygen (O_2), commonly called dry oxidation. This approach produced high-quality oxide layers but required high temperatures and prolonged processing times. Various liquid oxidants, like nitric acid and hot water, are introduced to avoid long processing times, resulting in a faster and more controlled oxidation

process. The nitric acid (HNO_3) oxidation of silicon produces silicon dioxide (SiO_2) and other by-products. The depth and nature of the oxide layer that forms on the silicon surface depend on the temperature and length of the immersion. HNO_3 oxidation is frequently combined with other techniques, such as dry/steam oxidation.

EXPERIMENTAL

Czochralski M2 (156.75x156.75mm^2) n-type wafers with a base resistivity of 2.25 Ω cm and bulk lifetime of around 1 ms from Longi solar were laser cut into 50 mm circular wafers. The wafers are categorised into two surface orientations, i.e., (1 0 0) after saw damage etch and (1 1 1) textured by KOH solution [2]. The (1 1 1) wafers are transferred into an automated wet bench for cleaning, etching the native oxide (SiO_2) layer, and for wet chemical oxidation. The two steps of RCA (Radio Corporation of America) cleaning procedure SC-1 and SC-2 are performed. SC-1 etch composed of NH_4OH (28 - 30%), H_2O_2 (30 %), and deionised (DI)-water (18.2 MΩ cm) in proportions of 1:1:5 is used at room temperature for 10 minutes to remove the organic residues.

Following the SC-1 etch, the wafers are rinsed in a DI-water (1 MΩ cm) bath for 2 mins [3, 4]. The inorganic or metallic residues are removed using the SC-2 etch, composed of HCl (37 %), H_2O_2 (30 %), and DI-water (18.2 MΩ cm) in proportions of 1:1:5 for 15 minutes

at 85°C. The cleaned wafers are rinsed in DI water (1 MΩ cm) once more for 2 mins [5, 6]. The native SiO_2 layer, or formed during RCA, is removed by etching the wafers in HF (48 %) with DI-water (18.2 MΩ cm) in the ratio 1:10 for 45 seconds or with NH4F (40 %) solution for 3 min [7]. The etched wafers are rinsed in the DI-water (0.013 MΩ cm - 0.1 MΩ cm) for 2 min. The rinsed wafers are dried by Nitrogen gas (4.7) with a purity (99.997 %) for about 5 - 10 seconds.

The dried wafers are treated with wet chemical oxidations (HNO_3/H_2O). HNO_3 oxidation, also known as the NAOS (Nitric Acid Oxidation of Silicon) method, is performed [8 - 11]. HNO_3 (65 % wt) is heated to 100°C for 30 min, and the wafers are dried by nitrogen gun for 1 min. The chemical reaction is as follows:

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O \qquad (1)$$

As a result of HNO3 oxidation, a thin layer of SiO_2 is formed. On half of the wafers, the additional wet hydrogenation step is performed. On the other half, the dry hydrogenation process is carried out. The overview of the experimental conditions is shown in Table 1. The carrier lifetime of a pair of wafers is measured for each combination. During each experimental step, single-side polished wafers with orientation (1 1 1) are used to measure the thickness of the SiO_2 layer (see Table 2) by spectral ellipsometry by J. A Woolam 2000 ellipsometer [5].

The photoconductivity experiment using the Sinton

Table 1. All the combinations of the experimental conditions.

Orientation	Cleaning	Oxide Etch		Oxidation	Hydrogenation	
(111)	RCA	HF	Nitrogen Drying	HNO_3	dry	Nitrogen Drying
					wet	
					-	
				Hot water	dry	
					wet	
		NH_4F		HNO_3	dry	
					wet	
					-	
				Hot water	dry	
					wet	
(100)	RCA	HF		HNO_3	wet	
					-	
		NH_4F		HNO_3	wet	
					=	

WCT-120 lifetime tester determines the excess carrier lifetime. Throughout each process step, the lifetime, which is the effective lifetime (τeff) of the sample and its stability over time, is monitored, and an average value for each sample pair is taken. For the wafers of a sufficiently high bulk lifetime, the τeff is dominated by the contribution from surface recombination given by surface recombination velocity (S) and thickness (W) according to equation (2). This equation is valid as the measured values are at least an order of magnitude smaller than the bulk lifetime of 1 ms.

$$\tau eff \cong W/2S \qquad (2)$$

The photoconductivity for the reference wafer is shown in Fig. 1. The reference wafer (polished p-type wafer) has a thickness from 500 to 550 µm and a base resistivity from 1 to 10 Ω-cm is used to determine the photoconductivity. The photoconductance (Siemens) and light intensity (suns) as functions of time are shown in Fig. 1(a). The Quasi Steady State Photoconductance (QSSPC) method is being used. The light intensity must be smooth and exponentially decaying in order to determine the sample's effective lifetime. Fig. 1(b) displays the carrier lifetime as a function of excess carrier density. The graph measures the carrier lifetime at the provided carrier density, the carrier density may vary depending on the method utilised in calculating the lifetime.
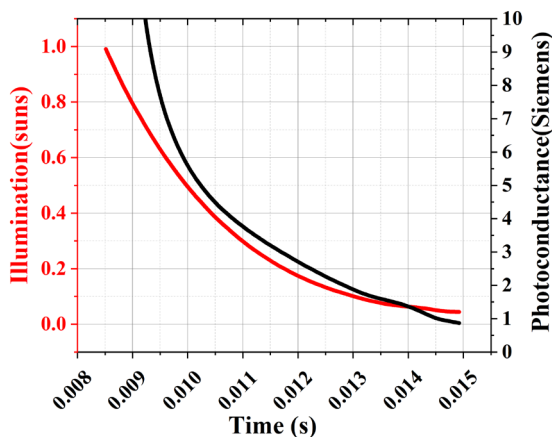
Table. 2. Thickness of SiO_2 measured after each step for the case of (1 1 1) orientation.

Process	SiO_2 Thickness (nm)
Native oxide	1.62 ± 0.5
RCA+HF	0.4 ± 0.5
After oxidation	2.04 ± 0.5

RESULTS AND DISCUSSION

Following the RCA cleaning process, Fig. 2 illustrates the effect of two different etching techniques performed on the (1 1 1) and (1 0 0) oriented wafers. Irrespective of the wafer orientation, Fig. 2 shows that the surface passivation is considerably higher immediately after HF etching and nitrogen drying than NH_4F etching. After roughly one day, τeff drops to values around 2µs. The impact of different etching techniques on the wet chemical oxidation is shown in Fig. 3. In the current instance, the carrier lifetime is all similar with a weak trend of slightly higher values for the (1 1 1) oriented wafers in HF etching solution. This is due to the high etching rate, selectivity, and uniformity of HF etching. To understand the HNO_3 (65 wt. %) oxidation temperature effect, an optimisation experiment is performed with the oxidation time kept constant, and the results are presented in Fig. 3. The trend indicates that the oxidation performed at 100°C gives the best carrier lifetime.
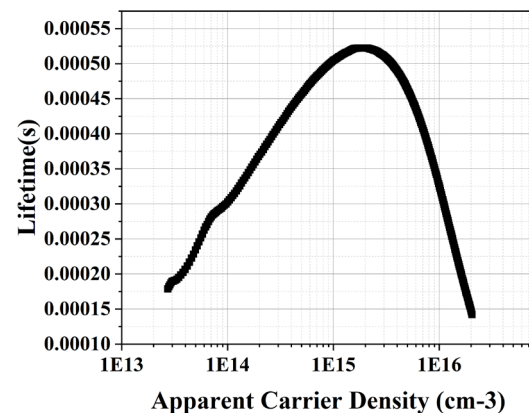

Fig. 1(a). Represents the photoconductance and Illumination with respect to time.

Fig. 1(b). Represents the lifetime with respect to carrier density.
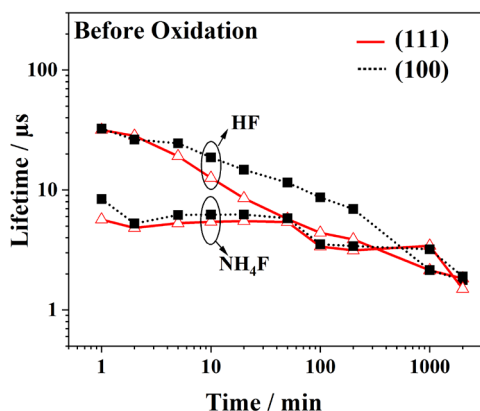
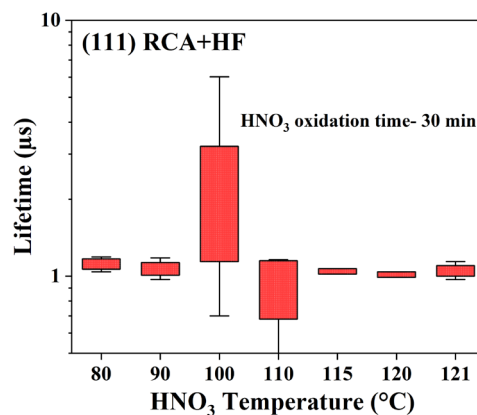Fig. 2. Effect of etching (HF, NH₄F) process prior to the wet chemical oxidation of wafers.

Fig. 3. Effect of different oxidation temperatures on HF etched wafers.

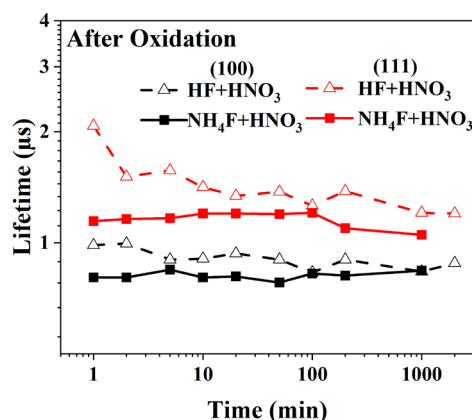Fig. 4. Effect of HNO₃ oxidation on HF and NH₄F etching process.

However, looking at Fig. 4, whether the quality of oxide passivating is questionable. In the reality of TOPCon or POLO technology, the silicon oxide is combined with field effect passivation provided by a doped polycrystalline layer and also by hydrogenation step provided by deposition of SiNx layer from silane/ ammoniac mixture and firing. An original procedure of wet hydrogenation is carried out to provide hydrogenation. The wafers that underwent the wet hydrogenation procedure have a much longer carrier lifetime than those obtained immediately after the HNO3 or H2O oxidation process.

To observe the effect of different orientations and to understand how the wet hydrogenation affects the carrier lifetime of the wafers, see the trends in Figs. 5 and 6. We see that the carrier lifetime after wet hydrogenation is more than an order of magnitude higher for a relatively long period before decreasing and dropping back to 1 μs and there is not much difference between (1 1 1) and (1 0 0) wafers that were etched (45 seconds) by HF. Fig. 6 illustrates how the wet hydrogenation affects the NH₄F etched (3 min) wafers. Note that no principal difference is observed between (1 1 1) and (1 0 0) wafers.

Alternatively, to the wet hydrogenation, we used dry hydrogenation by SiN$_x$:H layer, deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) and firing at 800°C at a speed of 470 cm min^{-1}. Hydrogen in the SiNx:H layer diffuses towards the Si/SiO₂ interface. As shown in Fig. 7 and Fig. 8, dry hydrogenation gives a considerably higher carrier lifetime that is perfectly stable in time. The stability is most likely provided also by the SiNx capping layer. Figs. 7 and 8 illustrate the effect of the HF vs. NH₄F etching process before the HNO₃ oxidation. We can observe that the wafers that underwent HF etch always have a higher carrier lifetime than those that are NH₄F etched.

Fig. 9 (a) illustrates the effect of carrier lifetime on different types of oxidations with HF and NH₄F etch-processed wafers. Interestingly, the carrier lifetime increased even more and remained stable after the dry hydrogenation process when subjected to H₂O oxidation. This is due to the higher number of -H bonds present compared to the HNO₃ oxidation. On the other hand, Fig. 9(b) indicates that hot water oxidation gives a superior carrier lifetime followed by dry hydrogenation and performs poorly after wet hydrogenation.
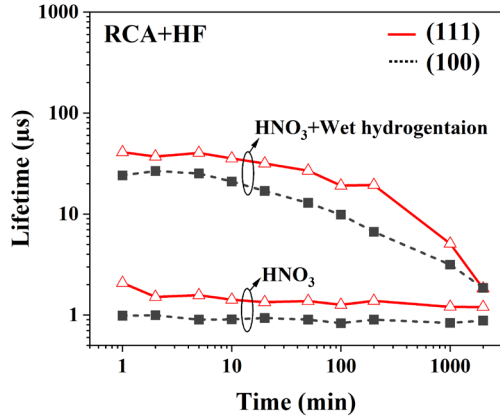
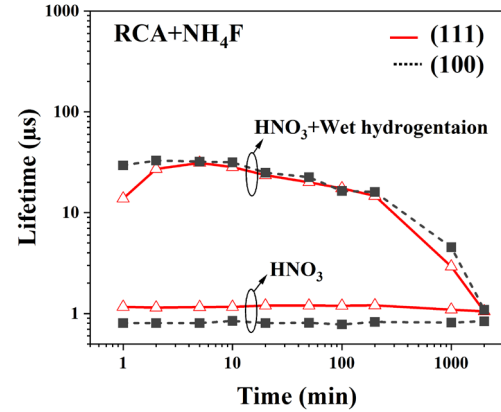Fig. 5. Effect of wet hydrogenation after HF etch and oxidation.

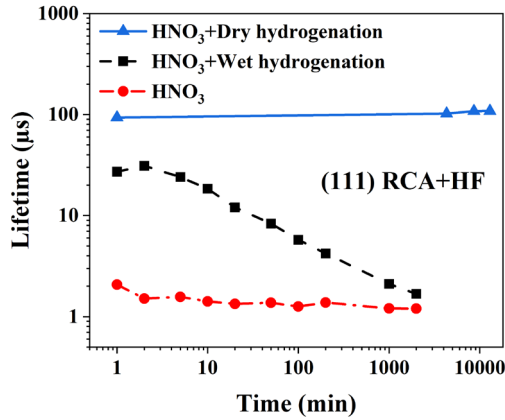Fig. 6. Effect of wet hydrogenation after NH_4F etch and oxidation

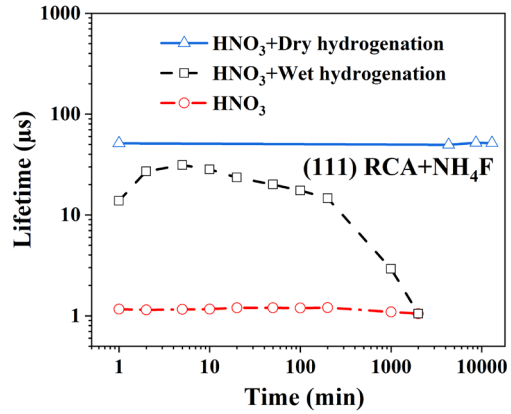Fig. 7. Effect of HF etching on dry, wet hydrogenation and HNO_3 oxidation.

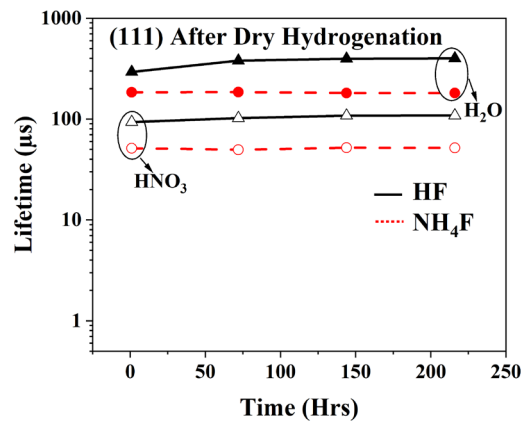Fig. 8. Effect of NH_4F etching on dry, wet hydrogenation and HNO_3 oxidation.

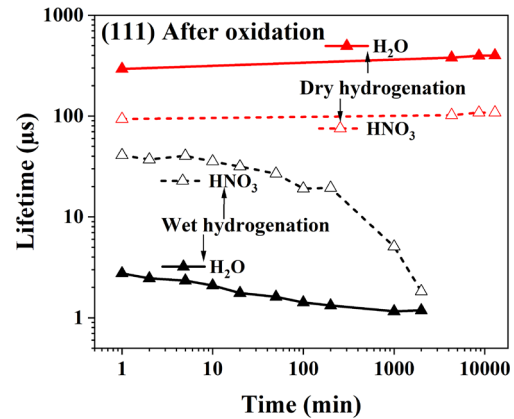Fig. 9(a). Effect of type of oxidation process on the lifetime after dry hydrogenation.

Fig. 9(b). Effect of type of oxidation process combined either with dry or wet hydrogenation.

CONCLUSIONS

The carrier lifetime following HNO_3 and H_2O oxidation is relatively low, which suggests that the SiO_2 layer produced is highly defective. An original process of wet hydrogenation after oxidation, when tested against the standard dry hydrogenation process, the carrier lifetime was more than an order of magnitude higher than the carrier lifetime obtained after HNO_3 and H_2O oxidation. Interestingly, the carrier lifetime value does not depend much on the type of native oxide etching and the surface orientation but strongly depends on the method of re-oxidation. Another benefit of wet hydrogenation is the carrier lifetime's temporal stability, which is considerably improved, especially for the HF etched Si (111) surface, which is probably the most relevant for future industry. Furthermore, when using standard dry hydrogenation, it is observed that H_2O oxidation gives almost an order magnitude higher values when compared to the wafers that underwent HNO_3 oxidation. This is quite the opposite of the wafers that underwent wet hydrogenation after HNO_3 and H_2O oxidation. It can be concluded that in the case of dry hydrogenation, irrespective of the HF or NH_4F etch, water oxidation is the most suitable process to grow the oxide layer. This high lifetime stability provides the benefit of using the textured wafers on the rear side of the TOPCon structures.

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