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RESEARCH PAPER

Multicrystalline Silicon Passivation by Hydrogen and Oxygen-Rich Porous Silicon Layer for Photovoltaic Cells Applications

Aqeel Mohammed Hamoudi[1], Karim Choubani[2], Mohamed Ben Rabha[1,*]

* *rabha2222@yahoo.fr*

[1] Research and Technology Centre of Energy, Tunisia
[2] College of Engineering, Imam Mohammad Ibn Saud Islamic University, Riyadh, Saudi Arabia

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Abstract: *In this work, we demonstrate the beneficial effect of introducing a superficial porous silicon layer on the electronic quality of multi-crystalline silicon for photovoltaic cell application. The porous silicon was prepared using an acid vapor etching-based method. The porous silicon layer rich in hydrogen and oxygen formed by vapor etching using an excellent passivating agent for the mc-Si surface. Laser beam-induced current (LBIC) analysis of the exponent parameter (n) and surface current mapping demonstrated that oxygen and hydrogen-rich porous silicon led to an excellent surface passivation with a strong electronic quality improvement of multi-crystalline silicon. It was found that the generated current of treated silicon by acid vapor etching-based method is 20 times greater than the reference substrate, owing to recombination centers passivation of the grains and grain boundaries (GBs); The actual study revealed an apparent decrease in the recombination velocity of the minority carrier as reflected by 25% decrease in the exponent parameter (n) of the LBIC versus X-position measurements. The results obtained for the prepared porous silicon in this study indicates its possible use in a more efficient photovoltaic cell applications.*

Keywords: *Multi crystalline silicon, Laser beam induced current, Vapor etching, Oxygen and hydrogen, Passivation.*

1. INTRODUCTION

Technological advances have recently improved efficiencies in multi-crystalline silicon (mc-Si) photovoltaic cells, making them a popular choice for solar panel manufacturers. Mc-Si is a very attractive material due to its low wafer cost compared to monocrystalline silicon (c-Si) [1, 2]. The random orientation of crystals in mc-Si can lead to defects and impurities, reducing the efficiency of solar cells made from this material. In addition, the grain boundaries between the individual crystals can act as recombination centers for charge carriers, reducing the cell's overall efficiency. They can be improved by utilizing oxygen and hydrogen passivation of crystal defects [3-5]. Compared to monocrystalline silicon (c-Si), which has a higher efficiency due to its single, continuous crystal structure, mc-Si typically has a lower efficiency. However, mc-Si is also less expensive to produce than c-Si, which makes it a more cost-effective option for many solar panel manufacturers. Additionally, ongoing research and development in the field of mc-Si technology may lead to further improvements in efficiency and performance in the future [6, 7]. Previous research has shown that mc-Si passivation using oxygen and hydrogen-rich porous silicon can improve its electronic quality and enhance the efficiency of photovoltaic cells made from this material [8, 9].

This study aims to investigate the effectiveness of a superficial porous silicon layer formed using an Acid Vapor Etching-based method for passivating the mc-Si surface. This method has advantages over other techniques due to its low cost, simplicity, and compatibility with industrial processes. To assess the quality of the passivation layer, we carried out various characterization techniques, including Laser Beam-Induced Current (LBIC) analysis, IR reflectivity, absorption, and two-dimensional internal quantum efficiency measurements. These techniques allow us to determine the effect of the oxygen and hydrogen-rich porous silicon on the optoelectronic quality of the mc-Si and the reduction in recombination centers for charge carriers at the grain boundaries. The results of our study have implications for the development of more efficient and cost-effective photovoltaic cells.

2. MATERIALS PROCEDURES

P-type mc-Si wafers with a resistivity 0.5-2 Ω.cm and thickness of 330 µm were used in this work. Oxygen and Hydrogen-rich porous silicon were achieved by Acid Vapor Etching (AVE) [10] with a silicon wafer. This technique consists of exposing the mc-Si substrates to vapor issued from a mixture acid solution of HNO_3: HF, figure 1 shows the SEM images of mc-Si nanostructures obtained after AVE.

3. RESULTS AND DISCUSSION

In order to assess the effectiveness of the passivation treatments using oxygen and hydrogen-related complexes, the electronic quality of the mc-Si before and after acid vapor etching must be examined. To this end, the LBIC method has been used, which involves scanning the mc-Si surface with a laser beam to measure the generated current, as shown in Figure 2. Specifically, a 632 nm wavelength He-Ne laser for the excitation spot has been operated.

To obtain further insight into the passivation effect of oxygen and hydrogen-rich porous silicon on the electronic quality of mc-Si, the surface recombination velocity (SRV) was calculated using the exponentiation parameter (n) from LBIC measurements. The experimental data were fitted to theoretical models assuming a semi-infinite semiconductor and high X-positions, far from the edge of the collector, as reported in previous works that also used LBIC analysis [11, 12]. The value of n reflects the surface recombination velocity and provides essential information on the effectiveness of the passivation layer is given by the relation 1:

$$I_{LBIC}(x) = B * x^{-n} \quad (1)$$

Where: x is the distance from the Ag/Al grid contact and the laser beam, B is constant depending primarily on the beam intensity, and the penetration depth and n is related to the surface recombination velocity (SRV). The parameter n varies between 0.5 for SRV= 0 and 1.5 for SRV= ∞: in this case, the electronic quality of the mc-Si wafer is good if the exponential parameter n is close to 0.5. At high X-positions, a power law predominates and from which we can estimate the exponentiation parameter (n) and determine the effectiveness passivation of mc-Si treatment.

The results of the Exponential parameter (n) estimation for untreated and treated samples using MATLAB Curve-Fitting are summarized in Table 1. At the same time, the measured and simulated induced current profiles related to mc-Si before and after AVE are shown in Figure 3.

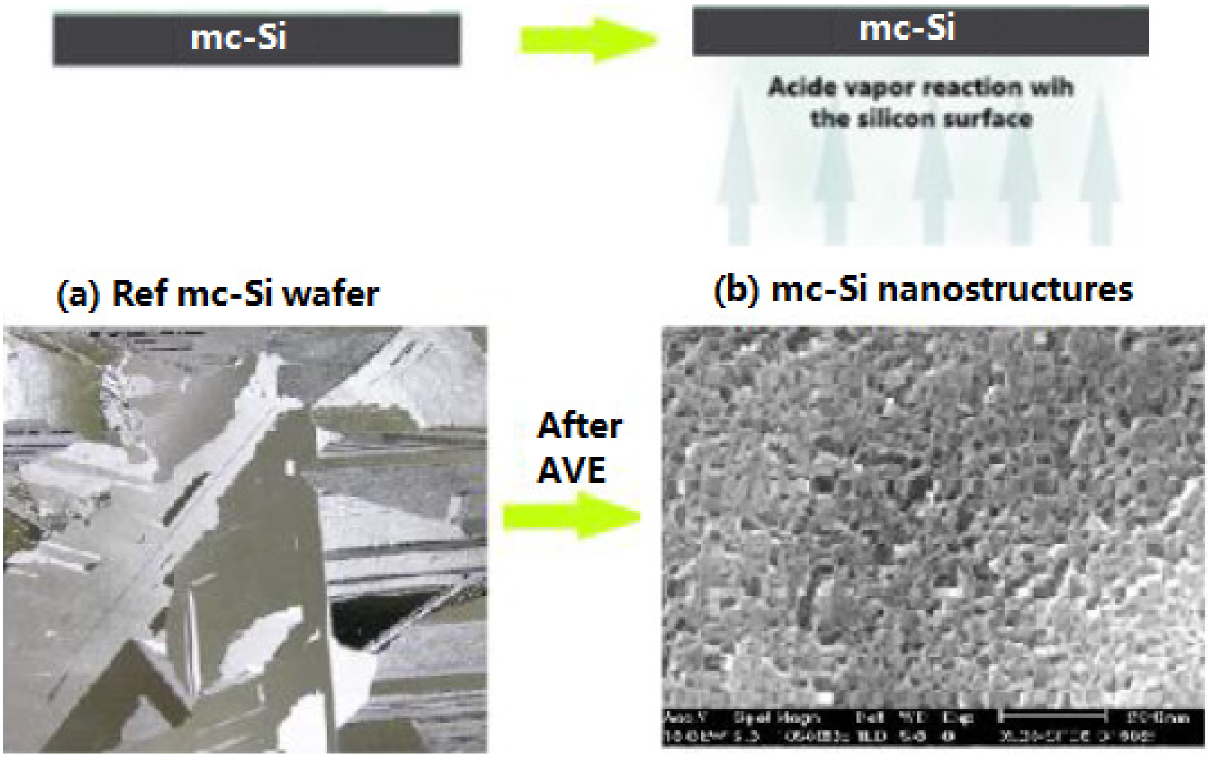

Fig. 1. SEM images of mc-Si nanostructures obtained after AVR

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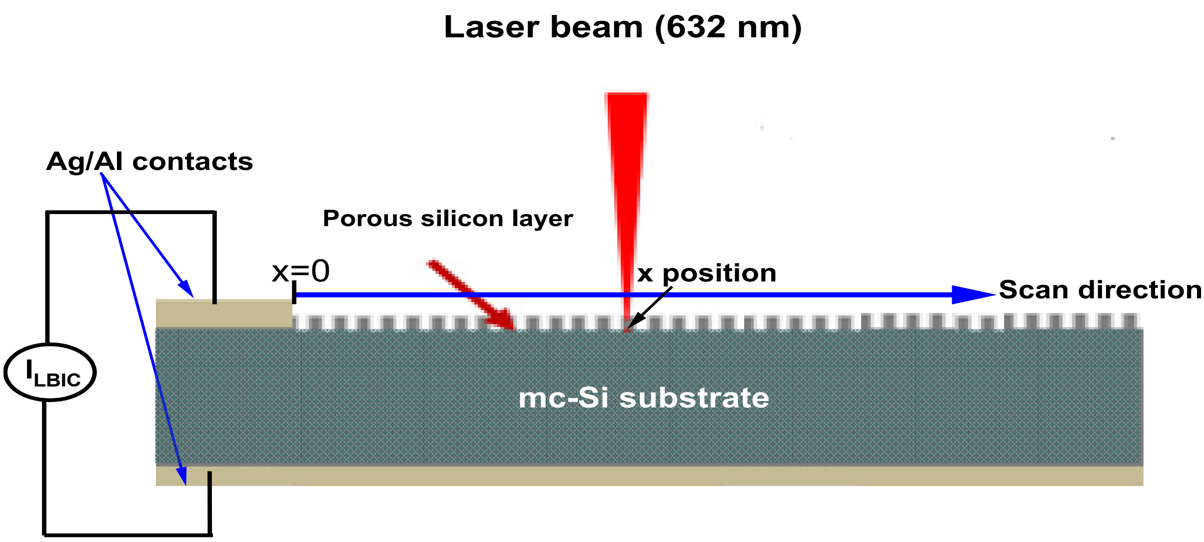

Fig. 2. LBIC technique to measure current by scanning mc-Si surface

Table 1. Exponent parameter (n) estimates for untreated and treated samples by AVE

Fit Model $f(x) = B * x^{-n}$	**B**	**95% confidence bounds**	**n**	**95% confidence bounds**	R^2
Untreated	138.4	(115.8, 160.9)	0.9684	(0.9476,0.9891)	0.9747
Treated	29.2	(23.32, 35.08)	0.728	(0.7026,0.7533)	0.931

The obtained results of Exponent parameter (n) for untreated 0.97 and treated 0.73 samples indicate a significant improvement in the purity of the silicon after treatment due to the reduction of the surface recombination velocity and to the electronic quality improvement.

Figure 4 displays the FTIR spectra obtained after forming porous silicon by AVE, which reveal two influential bands. The first absorption peak, observed at wave numbers 1025-1160 cm^{-1}, is attributed to oxygen complexes, specifically Si-O stretching modes in O-Si-O and c-Si-O. The second band, present at wave numbers 2050-2260 cm^{-1}, is attributed to Si-H stretching modes of $Si-H_x$, where x= 1, 2, and 3. As per reference, the absorption peaks observed at wave number 1427 cm^{-1} can be assigned to the N-H bonding group [14]. It is also worth noting that the XPS spectra contribute to the FTIR spectrum, as mentioned in [15, 16]. Based on the FTIR spectra presented in Figure 4, samples with higher concentrations of O and H exhibit both bands specific to hydrogen and oxygen-related complexes (see Table 2).

The efficacy of hydrogen and oxygen passivation of mc-Si silicon wafers has been confirmed to decrease surface recombination velocity and enhance electronic quality significantly. This is crucial in diminishing non-radiative Si dangling bond defects. After AVE treatment, the exponentiation (n) decreases by a whopping 25 % from 0.97 to 0.73, indicating the exceptional electronic quality of the mc-Si substrate. These findings unequivocally demonstrate the high efficiency of the passivation process in improving the substrate's electronic properties [17].

In the IR absorption spectrum, the integrated intensity of hydrogen and oxygen, were deduced by the relation 2 [18]**:**

$$I = \frac{N}{A} = \int \alpha(\omega)/\omega \, d\omega \qquad (2)$$

N, A, ω and α in the above equation are, respectively, the concentration, the proportionality constant, the wave number and the absorption coefficient. In figure 5, we give the two-imensional Internal Quantum Efficiency (IQE) distribution figure .5a before and figure .5b after PS treatment using the LBIC technique.

One may notice that the IQE varies between 25% and 35% for mc-Si wafers without PS. However, after PS treatment, the minimum value of the IQE of the mc-Si wafer becomes 55%, and the maximum value reached 65% (which represents an increase of about 30%). Recorded to [19], two-dimensional Generated Current I_{LBIC} distribution before AVE and after AVE were illustrated in Figure 5.

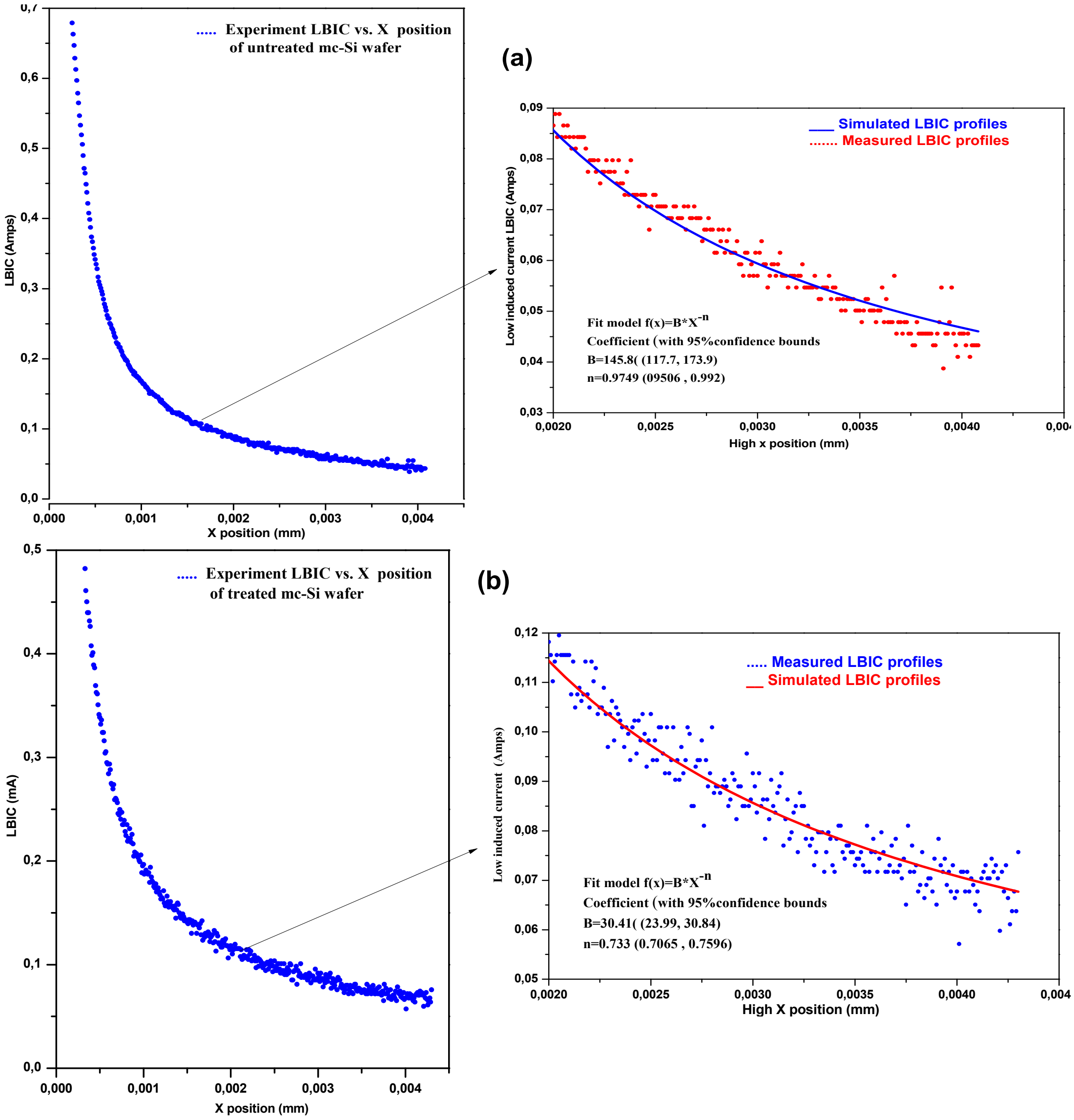

Fig. 3. a) LBIC profiles for untreated mc-Si b) AVE-treated mc-Si. Full lines correspond to theoretical simulation.

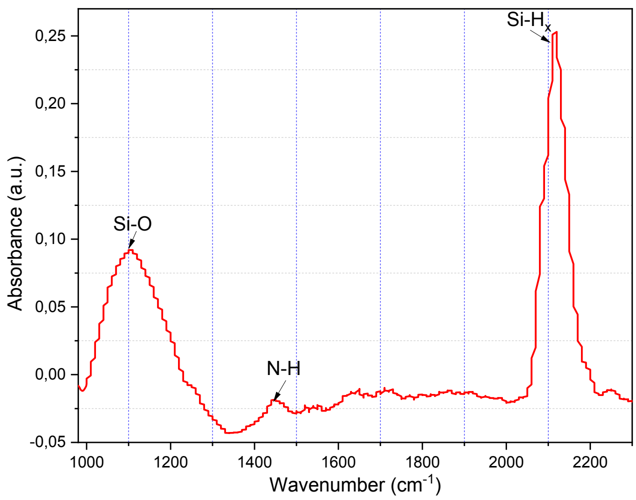

Fig. 4. FTIR spectra after porous silicon formation (spectra of the untreated sample as a reference)

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Table 2. Oxygen and hydrogen integrated intensity from FTIR spectrum before and after mc-Si AVE

mc-Si	Integrated intensity of oxygen in cm^{-1}	Integrated intensity of hydrogen in cm^{-1}
Before	0	0
After	0.008	0.012

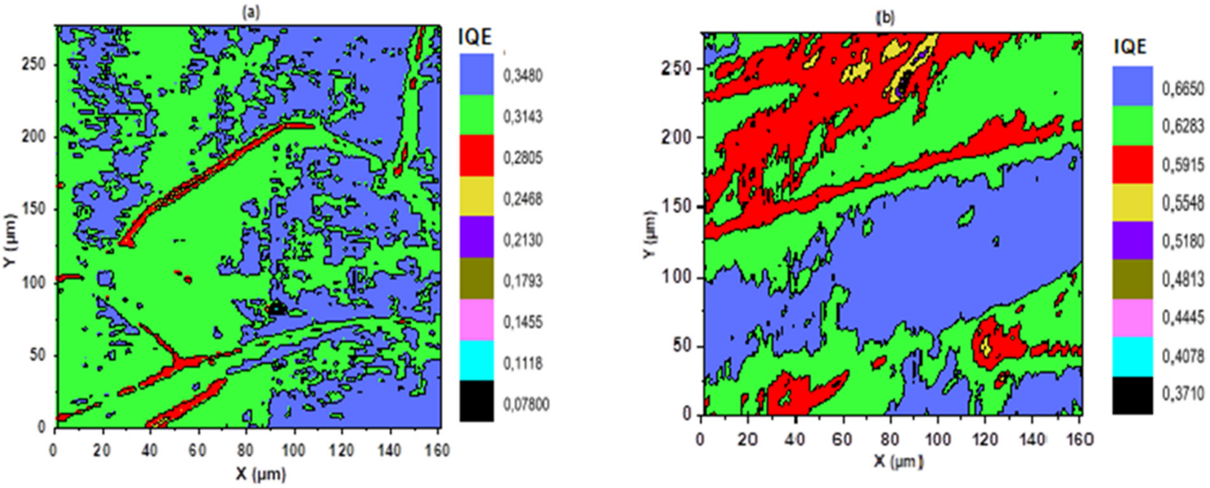

Fig. 5. 5. a) Two-dimensional IQE distribution before PS b) after treatment using the LBIC technique

A significant variation in the Generate Current due to variations in the defects' density has been detected. Moreover, an enhancement of the I_{LBIC} after AVE was observed compared to untreated mc-Si; in this case, the measured I_{LBIC} varied between 21 nA to 47 nA (figure 6b), while the Generate Current varied between 4.98 nA to 9.52 nA for untreated mc-Si (figure .6a), this progression in the measured current I_{LBIC} can be explained by the reduction of the surface recombination velocity and to the electronic quality improvement due to recombination centers passivation at the grains and GBs.

Indeed, the disappearance of the dark areas in both grain and grain boundaries of mc-Si has been observed. Therefore, this disappearance can be ascribed to the diminution of defects' density as a consequence of the hydrogen and oxygen passivation effect [20-24].

A significant decrease in reflectivity was observed in figure 7 and reached 3% after AVE, compared to 38% for untreated mc-Si, the result of the change in the mc-Si surface morphology and its similar to silicon nanowire's structure [20], it has a direct effect of the minority carrier diffusion length [21].

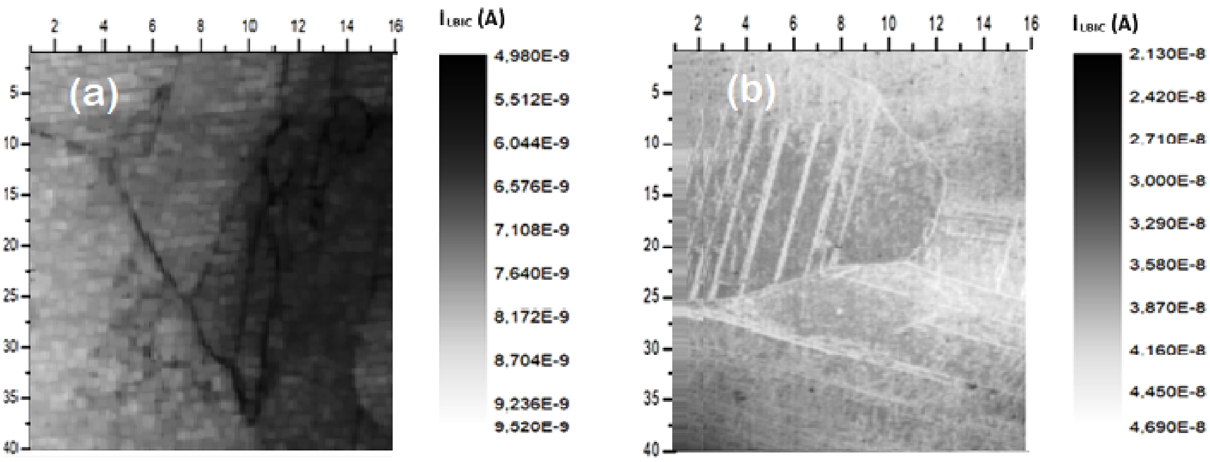

Fig. 6. a) Two-dimensional Generated Current ILBIC distribution before AVE max value 9.5 10-9 A b) after AVE max value 46.9 10-9 A.

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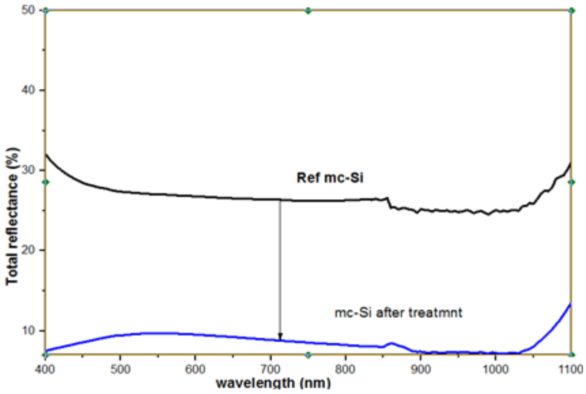

Fig. 7. Total reflectivity of mc-Si surface before and after AVE

4. CONCLUSIONS

The study utilized Acid Vapor Etching to create oxygen and hydrogen-related compounds to improve the surface passivation and electronic properties of multi-crystalline silicon wafers. The results demonstrated substantial improvements in Generated Current mapping, surface recombination velocity, and IQE measured by laser beam-induced current. The presence of these compounds in silicon led to a 30% increase in IQE and a 25% decrease in the exponent parameter (n), indicating a reduction in recombination velocity. This research has important implications for developing more efficient and cost-effective solar technologies and future photovoltaic cells. The findings provide insights into the effectiveness of Acid Vapor Etching in improving the electronic properties of multi-crystalline silicon wafers. They can help pave the way for further research in this area. Overall, this study represents a significant step forward in the field of solar cell technology and has the potential to contribute in creating more sustainable and environmentally friendly energy sources.

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