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Sulfurization as a promising surface passivation approach for both n- and p-type Si

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***Abstract*—Sulfur is demonstrated to be an effective and promising surface passivation element for both n- and p-type Si wafers after reacting in dilute hydrogen sulfide gas (2 – 6% in argon) at 550°C. Effective minority carrier lifetimes of > 2 ms and > 0.25 ms are achieved for n- and p-type Si wafers, respectively, comparable to the industry standard thermal oxide and atomic layer deposited aluminum oxide passivation level. Surface characterization by x-ray photoelectron and emission spectroscopy reveals that sulfur is primarily bonded in a sulfide environment.**

Keywords—Si surface passivation, sulfur, x-ray photoelectron spectroscopy, x-ray emission spectroscopy

I. Introduction

Si surface passivation has been the primary reason for the rapid increase of Si solar cell efficiency to >25 % by improving the open circuit voltage (V_{OC}) over the past decade. Surface recombination has become even more critical with the manufacturing development of thinner industrial Cz-grown wafers with higher bulk quality, now being the performance-determining process. All high V_{OC}, high efficiency Si solar cells employ one of the following three surface passivation materials: (a) thermally grown (~ 1000 °C) SiO_2, (b) low temperature (< 300 °C) deposited amorphous Si (a-Si:H), or (c) Al_2O_3 by atomic layer deposition (ALD). Each of these passivation structures has their own limitations. Thermal SiO_2 is the most common method for Si surface passivation, but the high temperature process creates difficulties to maintain high bulk quality. Si heterojunction (HJ) solar cells with a-Si:H surface passivation have demonstrated high V_{OC}, but the passivation quality degrades severely at temperatures above 300 °C. This limits the downstream contact metallization process to < 300 °C. ALD-deposited Al_2O_3 has shown excellent passivation quality and has been successfully integrated in industrial p-type passivated emitter rear contact (PERC) Si solar cells. However, it works best for p+ diffused surfaces due to its negative charge induced passivation mechanism.

The chalcogen elements S and Se were theoretically predicted to terminate Si surface dangling bonds and thereby eliminate the surface states [1]. We have earlier shown that S can effectively passivate n-type Si surfaces with reduced surface states (interface defects) [2,3]. In this work, we have studied sulfur and its application as a passivation material for both n- and p-type industrial Cz Si planar and textured wafers, and compare the passivation quality with that of standard thermal SiO_2 and ALD Al_2O_3.

II. Experimental

n-type (bulk lifetime of ~ 5 ms) and p-type (bulk lifetime of ~ 0.5 ms) industrial Cz Si planar and textured wafers with a thickness of 160 µm and a resistivity of 2 Ω.cm were used in this work. The as-cut wafers were planarized and textured in KOH. Both planar and textured wafer surfaces were passivated by an H_2S (99.9 % purity) gas reaction at atmospheric pressure with varying reaction temperature (450 – 650 °C), time (15 – 210 mins), and H_2S concentration in Ar (0.5 – 6.5%). Details of the thermal H_2S CVD reactor are reported elsewhere [2]. Prior to

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the H_2S reaction, the wafer surfaces were treated and cleaned using the following steps: (1) surface etch in an acid mixture (HNO_3:HF = 100:1), (2) surface oxidation in piranha solution, and (3) removal of surface oxides in 10 % HF for 1 min, with 5 mins DI water rinse between each step. The surface passivation quality after H_2S reaction was evaluated by effective minority carrier lifetime (τ_{eff}) measurements using a Sinton quasi-steady-state photoconductance (QSSPC) lifetime tester. The τ_{eff} values are reported at an excess carrier density of 1×10^{15} cm^{-3} in this work. The surface and sub-surface chemical structure was studied on selected wafer samples with and without S passivation by x-ray photoelectron spectroscopy (XPS, using Mg K_α excitation and a SPECS PHOIBOS 150 MCD electron analyzer at UNLV) and x-ray emission spectroscopy [XES, at Beamline 8.0.1. of the Advanced Light Source (ALS), Lawrence Berkeley National Lab, using the SALSA endstation] [4], respectively. Sister wafers from the same batch were passivated by thermal oxide and ALD Al_2O_3 for comparison.

III. Results and Discussion

The τ_{eff} values were measured immediately after the samples were removed (~ 2 mins) from the H_2S reaction chamber. We did not observe any significant difference in τ_{eff} between planar and textured surfaces, but there is an obvious difference between n-type and p-type wafers. This is expected, because the n- and p-type wafers have different bulk lifetimes, and the τ_{eff} values include both bulk and surface lifetimes. Figure 1 shows the variation of τ_{eff} as a function of (a) H_2S reaction temperature and (b) H_2S gas phase concentration for the passivation reaction performed for 30 mins. For the temperature series, the H_2S concentration was fixed at 3.4% in Ar, and for the varying concentration series, the reaction was performed at 550 °C. Fig. 1(a) shows that the optimum passivation reaction temperature is found between 500 and 600 °C. Fig. 1(b) indicates that the τ_{eff} values are similar for H_2S concentrations > 1%. The results demonstrate that an excellent surface passivation, with $\tau_{eff} > 2$ ms for n-type and > 250 µs for p-type wafers, can be achieved at relatively low process temperatures using a very dilute H_2S gas phase reaction. Multiple passivation runs were conducted at 550 °C with 3.4% H_2S concentration on both planar and textured wafers, but did not exhibit any dependence on surface structure.

After establishing the optimum reaction temperature and H_2S concentration, a series of Si surface passivation treatments was performed for both n- and p-type wafers with planar and textured surfaces, with varying reaction time at 550 °C in 3.4% H_2S. Fig. 2(a) shows the variation of τ_{eff} as a function of reaction time. The passivation quality is almost independent of the reaction time range (15 to 210 mins). This result suggests that such passivation quality could possibly also be achieved by rapid thermal processing (RTP) for industrial application.

Although we have not observed any dependence of initial passivation quality on the reaction time, the rate of degradation in air appears to be dependent on the reaction time [Fig. 2(b)]. The passivation performed for a shorter time degrades at a faster rate than the longer reaction time, despite their similar initial τ_{eff} values.

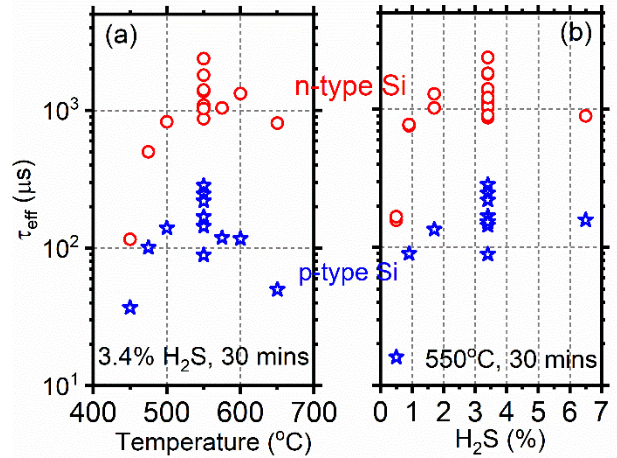

Fig. 1. Effective minority carrier lifetime (τ_{eff}) of the n-type (blue) and p-type (red) Cz Si wafers after surface passivation by H_2S gas phase reaction for 30 mins at (a) varying temperature and (b) varying H_2S gas phase concentration in Ar.

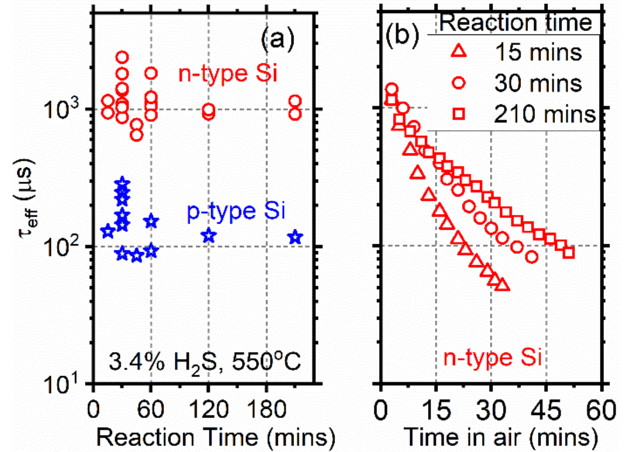

Fig. 2. Effective minority carrier lifetime (τ_{eff}) of the n-type (blue) and p-type (red) Cz Si wafers after surface passivation by 3.4% H_2S at 550°C for (a) different reaction duration and (b) after exposing the passivated samples to air.

The local chemical bonding environment at and near the surface after H_2S reaction were studied by XPS and XES. Figs. 3(a) and (b) show the XPS spectra of the S 2s and Si 2p regions, respectively, for both n- and p-type wafers after H_2S reaction ("passivated") and after 8 days of air exposure ("degraded"). The gray boxes represent binding energies commonly found for different chemical environments, including sulfur in a sulfide and S-O environment, and silicon in a Si and Si-O environment. The S 2s spectra clearly show that sulfur is predominantly found in a sulfide environment, with no substantial S-O bonds for an of the samples (a small S-O signal might be inferred for the p-type Si passivated sample). We note that the S 2s signals of the degraded samples are significantly smaller than for the passivated samples. We ascribe this to a loss in S surface coverage (e.g., by H_2S formation), which would "free up" Si surface atoms, formerly in a Si-S bond, to form Si-O bonds (see

below). Future XES experiments will need to be conducted to monitor potential Si-S bonds and their evolution during degradation.

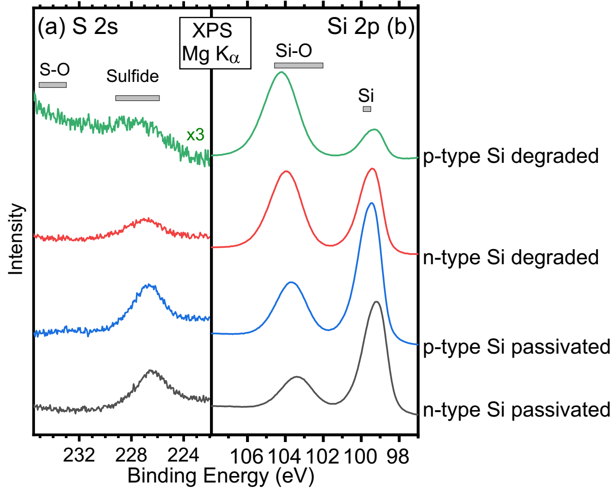

Fig. 3. XPS spectra of the (a) S 2s and (b) Si 2p core levels, indicating the surface chemical environment of n- and p-type Si in the passivated and degraded state. The S 2s spectrum of the p-type Si degraded sample is magnified by a factor of 3.

In contrast, the Si 2p spectra show elemental Si and Si-O bonds in the passivated samples. While the former intensity decreases, the latter increases for degraded samples. This again corroborates that Si-O bonds are formed by replacing Si-S bonds at the surface when the samples are exposed to air (degraded).

The chemical bonding environment of sulfur was further studied using S $L_{2,3}$ XES, utilizing the larger characteristic 1/e-attenuation lengths to also probe the bulk region near the surface. Fig. 4(a) shows the S $L_{2,3}$ emission of all four samples. The peak at ~ 148 eV [labeled (1) and due to the S 3s-derived valence band] indicates that all samples predominantly exhibit a sulfide bonding environment. However, when comparing with the gray bars labeled (2), S-O bonds can also be identified (except for the n-type passivated wafer), while they were very weak (if present at all) in the S 2s XPS spectra. The x-ray spectroscopy measurements thus suggest that the observed reduction of S-passivation quality in air is due to a decrease of S surface coverage and an ensuing Si oxidation process. A significant number of the Si-S bonds is thus replaced by Si-O bonds, and some S-O bonds are formed as well, even though the vast majority of the remaining sulfur atoms stays in a sulfide environment.

Such atmospheric oxidation processes and hence degradation of τ_{eff} can be effectively eliminated by capping the S passivated surface with a low-temperature (< 300 °C) plasma-deposited a-SiN_X, as shown in Fig. 5. The figure also shows that the a-SiN_X layer alone does not provide much surface passivation properties with $\tau_{eff} < 20$ µs.

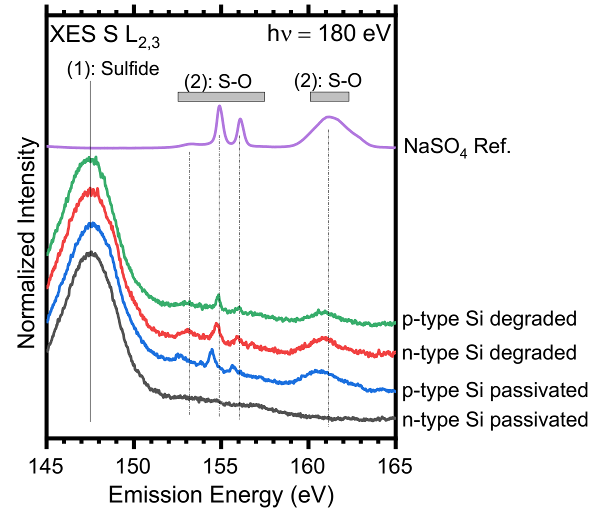

Fig. 4. S $L_{2,3}$ XES spectra of n-type and p-type Si, both passivated and degraded, and a sulfate reference.

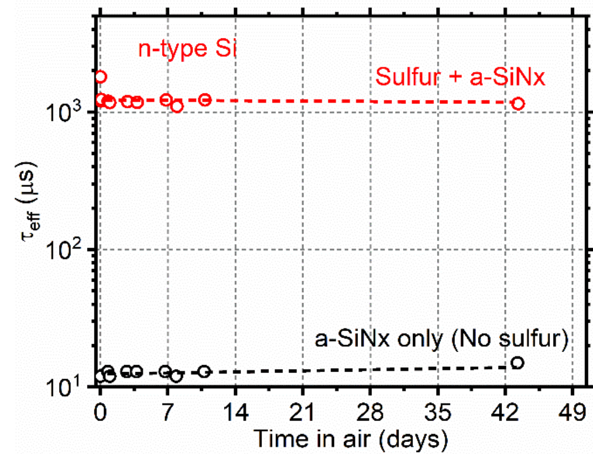

Fig. 5. Change in τ_{eff} of n-type Cz Si over time in air, after surface passivated by S and capped with a low temperature (<300 °C) deposited 80 nm a-SiN_X, and compared with τ_{eff} for a-SiN_X only.

Sister wafers from the same batch are passivated by industry standard thermal SiO_2 grown at ~850°C and by an ALD Al_2O_3 layer. These passivation structures were protected by a capping SiN_X layer. Table I lists the τ_{eff} and corresponding surface recombination velocities obtained by the as-grown oxides without any simulation firing, and compares the best passivation quality achieved by H_2S reaction at 550°C. The excellent passivation quality achieved after H_2S reaction demonstrates the suitability of S as a promising Si surface-passivating element for both n- and p-type wafers.

TABLE I. EFFECTIVE MINORITY CARRIER LIFETIMES AND SURFACE RECOMBINATION VELOCITIES OF N-TYPE AND P-TYPE SI WAFERS WITH SURFACE PASSIVATION BY THERMAL SiO_2, ALD Al_2O_3 AND H_2S REACTION.

	Effective minority carrier lifetime, τ_{eff} (µs)			**Surface recombination velocity (cm/s)**		
	Thermal SiO_2	**ALD Al_2O_3**	**H_2S reaction**	**Thermal SiO_2**	**ALD Al_2O_3**	**H_2S reaction**
n-Si	1690	2420	2370	3.1	1.7	1.8
p-Si	390	240	285	4.5	17.3	12.1

IV. CONCLUSION

Sulfur is found to provide a promising surface passivation for both n- and p-type Si wafers by reacting in dilute H_2S (2 – 6% in Ar) at 500 – 600°C. The chemical bonding environments at and near the surface, as studied by XPS and XES, features sulfur being primarily bonded in a sulfide environment, while air degradation is accompanied by a loss of sulfur surface coverage and the ensuing formation of Si-O bonds.

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