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An Isotope Study of Hydrogen Passivation of poly-Si/SiO_x Passivated Contacts for Si Solar Cells

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***Abstract* — Recent improvements in Si solar cell efficiency above 25% have used doped poly-Si/SiO_x or a-Si:H passivated contacts. Common to these designs is the need to passivate with hydrogen. In this contribution, we perform a systematic study of *p*-type poly-Si/SiO_x passivation by isotopic hydrogen using atomic layer-deposited (ALD) Al_2O_3 followed by an activating anneal.**

We observe that annealing *p*-type poly-Si/SiO_x in forming gas, or even nitrogen, is sufficient to provide some passivation. State-of-the-art implied open-circuit voltages exceeding 710 mV for *p*-type passivated contacts, however, were only achieved using Al_2O_3 and an activating anneal. This suggests that Al_2O_3 provides a superior source of hydrogen and diminishes the role of ambient hydrogen during the activating anneal.

I. Introduction

Crystalline silicon (c-Si) dominates the solar cell market [1], with diffused-junction solar cells holding the largest market share. On the other hand, all of the cells that have, in the past two years, improved on the previous Si solar cell efficiency record of 25.0% have used so-called passivated contacts as carrier-selective contacts [2], rather than diffusions, and it is to be expected that a future generation of high-efficiency c-Si modules will utilize this technology. In particular, passivated contacts based on polysilicon (poly-Si) / silicon oxide (SiO_x) stacks, have gained a lot of traction [3-6], with both Fraunhofer ISE and ISFH achieving 25% efficient Si solar cells using this approach [7, 8].

Hydrogen plays a pivotal role in achieving good chemical passivation of such passivated contacts, and is added after poly-Si deposition by many groups working on poly-Si/SiO_x passivated contacts to achieve the desired implied open-circuit voltage (iV_{oc}) values [9-11]. Interfaces between c-Si and SiO_2 can be hydrogenated using Al_2O_3 activated by an anneal [12], and Nemeth et al. have shown that this approach can also be successfully applied to poly-Si/SiO_x passivated contacts, and that the passivation persists even if the Al_2O_3 is etched off after the activating anneal [6]. In the following, we present a more systematic study of this process in order to understand the role played by the different process steps, using symmetric *p*-type poly-Si/SiO_x passivated contact lifetime samples and passivation by atomic layer-deposited (ALD) Al_2O_3:D and/or annealing in nitrogen or forming gas (FGA:D). Both Al_2O_3:D and FGA:D are deuterated, rather than hydrogenated, to permit follow-up secondary-ion mass spectrometry studies (SIMS) which will be the subject of a more detailed, upcoming publication.

II. Experimental Details

We prepared symmetric passivated contact structures as shown schematically in Fig. 1. As-sawn, 160 µm thick 3 Ωcm *n*-type Cz-Si wafers planarized in 25% KOH(aq) were RCA-cleaned [13] and had a 1.5 nm thick thermal oxide grown on them at 700°C in an N_2:O_2 mixture. Then, 20 nm boron-doped a-Si:H was deposited on both sides of the wafers, and subsequently crystallized by annealing in N_2 at 850°C for 30 min. Due to the consensus in the literature that *p*-type passivated contacts require more improvement than *n*-type passivated contacts [5, 6, 14, 15], this study focuses on the former.

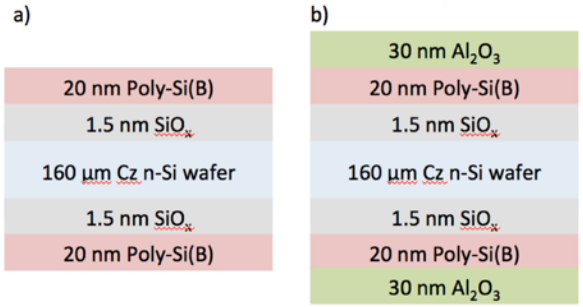

Figure 1. Schematics of samples prepared for this study.

Some samples were maintained as-crystallized (Fig. 1(a)), while others had 30 nm Al_2O_3:D deposited on both sides by thermal ALD using deuterated trimethylaluminum ($Al(CD_3)_3$) and heavy water as precursors (Fig. 1(b)). As-crystallized and Al_2O_3-coated samples were then exposed to 400°C anneals of different durations in nitrogen and/or deuterated forming gas (FGA:D). However, for simplicity, and because the final isotopic purity of these deuterated hydrogenation treatments is not accurately known at this stage, we will refer to hydrogen rather than deuterium throughout this manuscript. Photoconductance decay measurements performed with a Sinton WCT-120 lifetime tester in generalized (1/64) mode were used to derive iV_{oc} values and injection-level dependent minority carrier lifetimes.

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III. Results and Discussion

The iV_{oc} values obtained using lifetime samples prepared for this study are shown in Fig. 2(a),(b). We consider these to be sufficient to describe passivation because the injection-level dependent lifetime curves (shown for three representative samples in Fig. 2(c)) are all of the same shape, indicating that there is no fundamental change in recombination mechanisms upon passivation, merely a decrease in overall recombination rate by decreasing defect-mediated Shockley-Read-Hall recombination.

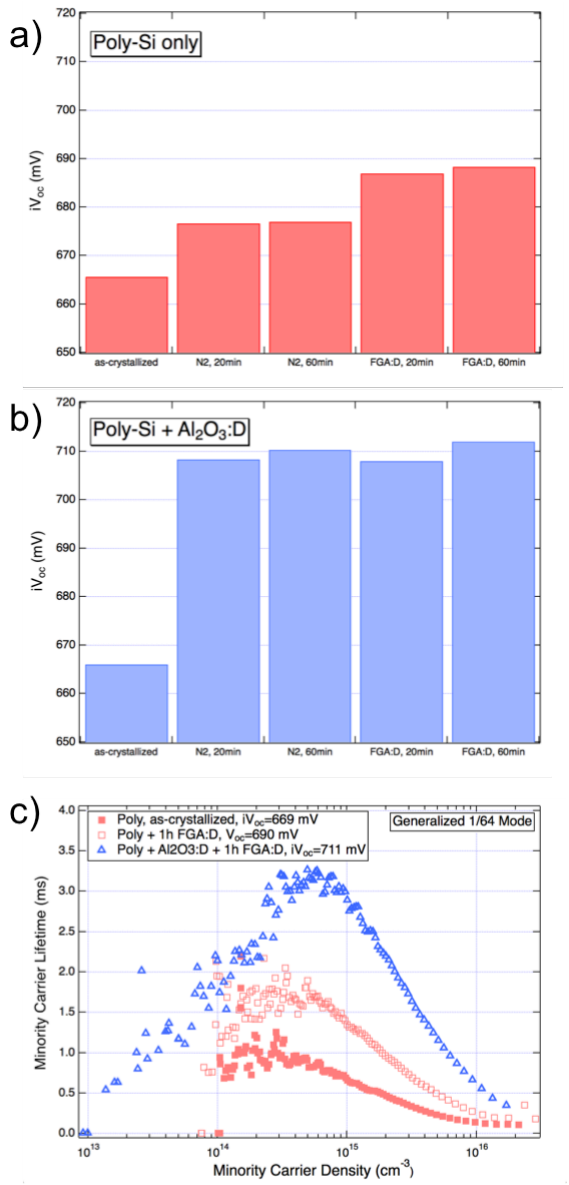

Figure 2: Implied open-circuit voltages of symmetric poly-Si(B)/SiO_x lifetime samples as a function of annealing treatment only ((a), samples as in Fig. 1(a)), and as a function of annealing treatment after Al_2O_3:D deposition ((b), samples as in Fig. 1(b)). Each data point represents the mean of three identically processed samples. Representative injection-level dependent lifetime curves from which these values are derived are shown in (c).

Figure 2(b) shows that state-of-the-art *p*-type passivated contacts have been prepared, exceeding 710 mV iV_{oc} after a 1 h activation anneal of the Al_2O_3:D at 400°C. More importantly, Figure 2(a) provides some clues as to what precisely happens within the material as symmetric poly-Si/SiO_x samples undergo passivation treatments; we observe an initial iV_{oc} of 667 mV that increases by ~10 mV upon 400°C annealing in nitrogen. This is rather unexpected: since the samples had previously been annealed at 850°C, and cooled slowly to room temperature thereby passing through the 400°C temperature regime, no additional changes are expected in a subsequent 400°C anneal. That said, we know from prior studies that as-crystallized samples do still contain some hydrogen. We therefore see two possibilities as to why passivation might improve upon nitrogen annealing: either hydrogen that had not effused from the a-Si:H upon crystallization becomes sufficiently mobile to passivate defects, or additional hydrogen originating from an unintended hydrogen background in the furnace tube diffuses into the sample and to the SiO_x/c-Si interface. Subsequently annealing the same samples in FGA:D increases iV_{oc} by another ~10 mV, which we attribute to the passivating effect of the additional hydrogen supplied by that annealing ambient.

Turning to samples on which Al_2O_3:D was deposited (Fig. 2(b)), we note that simply depositing it has virtually no effect: comparing the first bar in Fig. 2(a) and (b) shows that the iV_{oc} is only ~2 mV higher than on as-crystallized samples without Al_2O_3:D. This implies that the temperature of 200°C at which Al_2O_3:D is deposited is insufficient for hydrogen to diffuse through the poly-Si to the SiO_x/c-Si interface. 400°C, however, is sufficient, as is evidenced by the fact that post-annealing Al_2O_3:D at that temperature leads to a leap in $iV_{oc,}$ from below 670 mV to above 710 mV after 1h (Fig. 2(b)).

Interestingly, annealing in N_2 and FGA:D leads to similar results. This implies not only that FGA:D supplies negligible hydrogen compared to the Al_2O_3:D whose hydrogen it mobilizes, but also seems to indicate that effusion of hydrogen from Al_2O_3:D is not sufficiently detrimental to passivation of the SiO_x/c-Si interface for the difference in ambient partial pressure of hydrogen to have an effect. However, more in-depth studies involving compositional analysis will be required to validate this finding. In all cases, we observe some leveling off of the annealing effect after 20 mins, although small additional improvements in iV_{oc} are observed upon extending the treatment to one hour.

IV. Conclusion

We have performed a systematic study of *p*-type poly-Si/SiO_x passivation by isotopic hydrogen using atomic layer-deposited Al_2O_3 and nitrogen and forming gas anneals. We observed that annealing in forming gas, or even nitrogen, is sufficient to provide some passivation, which we attribute to hydrogen in-diffusion and/or activation of residual hydrogen within as-crystallized samples. However, state-of-the-art implied open-circuit voltages exceeding 710 mV were only

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achieved on the *p*-type passivated contacts studied here using Al_2O_3 in combination with an activating anneal. This suggests that Al_2O_3 provides a superior source of hydrogen and diminishes the role of ambient hydrogen during the activating anneal.

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