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Silicon Grain Boundary Passivation for Photovoltaics: A Novel Approach with Small Polar Molecules

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Abstract — Grain boundaries (GBs) play a major role in determining the device performance of in particular polycrystalline thin film solar cells including Si, CdTe and CIGS. Hydrogen passivation has been traditionally applied to passivate the defects at GBs. However, hydrogenated films such as amorphous silicon (a-Si:H) and microcrystalline silicon (c-Si:H) are subject to light-induced degradation effects. In this study on multicrystalline (mc)-Si wafers, we found an excellent correlation between the grain misorientation and the corresponding electrical resistivity across grain boundaries. In particular, the charge transport across GBs was greatly enhanced after the wafers were properly treated in our polar molecule solutions. The results were explained to be due to the more effective charge neutralization and passivation of polar molecules on localized charges at GBs. These findings may help us achieve high-quality materials at low cost for high-efficiency solar cells by improving the carrier transport and minimizing the carrier recombination. We also believe that this study will help us with a deeper understanding on GBs and their behaviors for the applications not only in photovoltaics, but also in other solid-state devices such as thin-film transistors.

Index Terms — grain boundaries, passivation, photovoltaic cells, silicon.

I. INTRODUCTION

Much interest has been shown in silicon thin-film solar cells because of their potential for low cost and other benefits such as non-toxicity and the essentially unlimited supply of basic materials [1, 2]. Among silicon thin-film technologies, polycrystalline silicon (poly-Si) (grain size: 1 μm to 1 mm) is a promising emerging technology. Poly-Si thin films have better transport properties and are not subject to light-induced degradation effects [1, 3], compared to hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon ($\mu\text{c-Si:H}$) films [4-6]. Rapid progress is being made and some promising results have been achieved in this field in the last several years. However, a lot of work still needs to be done before we see high penetration of polycrystalline thin film solar cells into the solar market. Grain boundaries (GBs) play a major role in determining the device performance of

polycrystalline thin film solar cells [7, 8]. To minimize the effect of GBs, the key is either to eliminate them or to eliminate their electrical activity [9, 10]. The latter approach of GB passivation is considered to be more feasible and economical. In this study, we therefore took a different approach using small polar molecules instead of hydrogen to passivate GBs in multicrystalline silicon (mc-Si) wafers. mc-Si wafers rather than poly-Si thin films were chosen because of their large grains, which make it much easier to study GB behaviors.

II. EXPERIMENTAL

Investigation was carried out on p-type mc-Si wafers (thickness: $\sim 200\mu\text{m}$; resistivity: 0.5-3 $\Omega\text{-cm}$; grain size: mm-cm). Wafers were first cut into small samples of a few cm. Specific investigated positions were slightly marked by a diamond scribe to check sheet resistivity changes before and after passivation. All samples were RCA cleaned using the standard procedure, followed by etching in 1:50 HF acid for 30 seconds, rinsing with deionized (DI) water for 1 minute, and drying with compressed air. The passivation was then conducted by immersing cleaned samples in methanol (CH_3OH), formic acid (CHOOH), acetonitrile (CH_3CN) and our ZK series polar molecule solutions, respectively, at a fixed temperature ($<100^\circ\text{C}$) for certain periods of time. Passivated samples were then taken out, dried with compressed air, and finally left in air at room temperature for more than 12 hrs before the sheet resistivity measurement with the four-point probe technique (Signatone S-301-4). The resistivity measurement was conducted under both dark and illuminated conditions. The light source was from a standard solar simulator (ABET Sun 2000). The sheet resistivity was measured both on bulk grains and across GBs. The average resistivity value at each position was obtained from a few data points. After each test, the sample was first RCA cleaned and then put back in the same chemical solution

for a longer period of time at an incremental step of five hrs to study the effect of passivation time on the resistivity. In addition, photoluminescence (PL) and electron backscattered diffraction (EBSD) techniques were also applied to study the correlation among the electrical, optical, and structural properties of GBs. For PL test, the wafer was illuminated by 810 nm light at an intensity equivalent to 1 sun and the data acquisition time was 600s. The plan-view EBSD mapping was carried out with an SEM microscope (Hitachi S-4300N) at 20 kV, a sample tilt angle of 70°, and a working distance of 15 mm. More details on PL and EBSD have been presented elsewhere [11].

III. RESULTS AND DISCUSSION

We first studied the GB passivation with pure polar molecular solutions only. Fig. 1 shows the sheet resistivity (R_{sheet}) across GBs vs. passivation time on two kinds of GBs — random and $\Sigma 3$ — under dark (D) and illuminated (L = light) conditions, respectively. The dipole moment of formic acid, methanol, and acetonitrile is 1.41 [12], 1.69 [13], and 3.9D [14], respectively (where D = Debye). As shown in Fig. 1 (a), methanol is effective in passivating random GBs. In particular after a 10-hr passivation, the dark and illuminated R_{sheet} decreased from 5637.2 and 3711.0 to 4317.2 and 3196.5 Ω/square , respectively (or decreased by 34.2% and 26.0%, respectively). However, the formic acid passivation on large-angle random GBs was not obvious at all. The dark and illuminated R_{sheet} remained around 5500 and 4800 Ω/square , respectively, with different treatment time. The passivation effect of acetonitrile is close to that of formic acid. As shown in Fig. 1(b), the passivation of each pure polar molecular solution on $\Sigma 3$ GBs does not change the resistivity a lot.

It is therefore shown that with appropriate polar molecules and periods of passivation, the electrical activity of some GBs can be reduced, which is true in particular to methanol whose molecule size is small [15] to make it easier for molecules to diffuse along GBs. However, the potential of each molecular candidate itself is still very limited in GB passivation. We then prepared three so-called ZK series solutions with the dipole moment ranging from 2.2 to 3.4 D.

As depicted in Fig. 2(a), each type of ZK solutions can reduce dramatically the sheet resistivity of random GBs. It is interesting to note that the GB R_{sheet} decreased from 5804.9 and 5083.6 to 1144.6 and 848.3 Ω/square , respectively, under dark and illuminated conditions with the treatment of ZK-22 for 5 hrs. Moreover, a 30-hr treatment resulted in further improvement that the dark

R_{sheet} reached 180.4 Ω/square and the illuminated R_{sheet} 176.2 Ω/square . The samples passivated in ZK-24 and ZK-42 exhibited similar trends. These findings are significant because it shows that the R_{sheet} of defective random GBs can be greatly reduced to be close to the bulk grain R_{sheet} (25-150 Ω/square) through simple passivation with small polar molecules. In addition, even after the passivated samples were left in air at room temperature for four weeks, the reduced resistivity remains almost unchanged. Also, we tested the conductivity of the three ZK solutions and ruled out the possibility that the GB resistivity reduction after passivation was due to the conductivity of passivation chemicals themselves. On the contrary, $\Sigma 3$ GBs are insensitive to the passivation, as shown in Fig. 2(b), which is similar to the cases shown in Fig. 1(b).

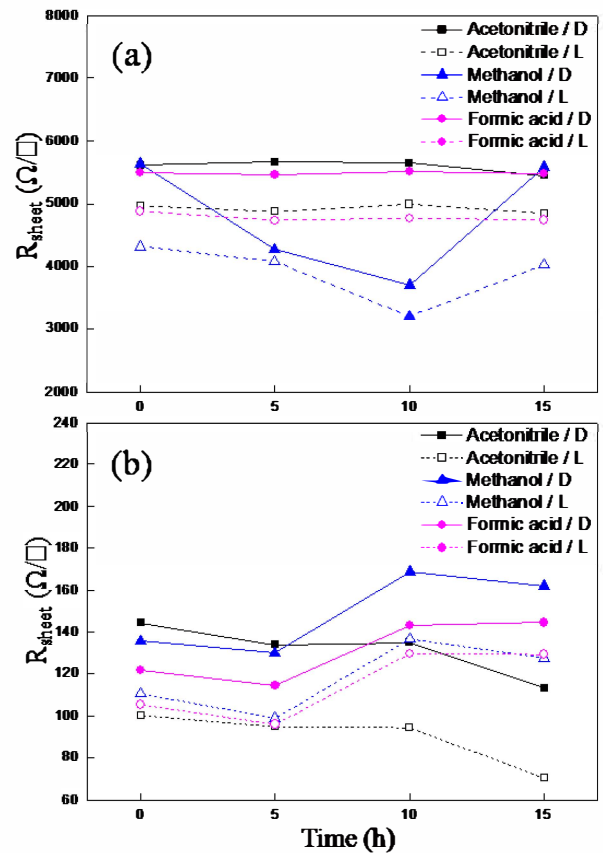


Fig. 1. Sheet resistivity (R_{sheet}) across GBs vs. passivation time of methanol, acetonitrile, and formic acid under dark (D) and illuminated (L) conditions, respectively. (a) Random GBs and (b) $\Sigma 3$ GBs.

Finally, we did EBSD for further study on the GB passivation with different recipes. Based on the PL results (not shown here), we selected a few typical GBs

according to their different sheet resistivity. The same GBs were studied by plan-view EBSD mapping to get grain misorientation between two adjacent grains. Fig. 3 indicates the EBSD maps of the sample passivated in ZK-22 for 30 hrs. The EBSD map is color-coded with the inverse pole figure (IPF) coloring in the sample normal direction Z_0 . Also shown is the grain misorientation (angle and axis of rotation) between adjacent grains. It is indicated that GB1 and GB3 are random GBs, whose electrical activity can be effectively passivated by polar molecules as shown previously. Whereas GB2, a $\Sigma 3$ coincidence site lattice (CSL) boundary, is in general immune to the same treatment. The corresponding dark R_{sheet} of each GB with different passivation time is listed in Table 1. It can be seen again that the ZK-22 solutions are in particular effective in passivating random GBs. These results are consistent with those reported in literature that hydrogen reduces the recombination activities at some GBs [8] [11] [16].

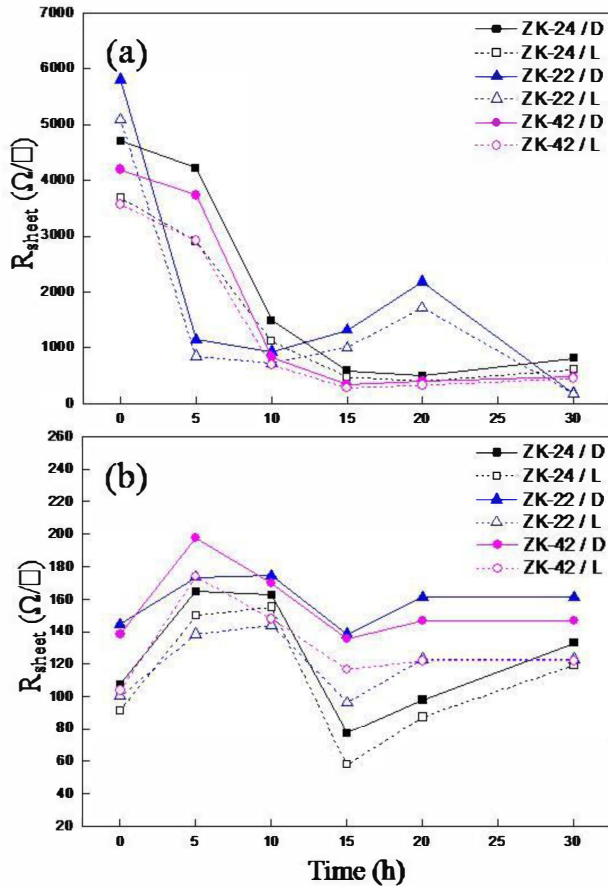


Fig. 2. Sheet resistivity (R_{sheet}) across GBs vs. passivation time of different solutions under dark (D) and illuminated (L) conditions, respectively. (a) Random GBs and (b) $\Sigma 3$ GBs.

In our recent study on upgraded metallurgical-grade silicon (UMG-Si) wafers, we showed that the optical response and GB structural properties were well correlated [11]. In the typical GB model [17], the trap states set up a potential barrier which opposes the immigration of charge carriers. Tsurekawa [18] indicated that the defect states are deeper at random boundary than at CSL boundaries, and random boundaries possess barrier heights almost twice as high as coincidence boundaries. In this study, we consistently observed that small polar molecules dramatically decreases the R_{sheet} of random GBs, which we think is closely related to the interaction between molecules and GB defects, including the possible charge redistribution along GBs after passivation. On the contrary, the activity of $\Sigma 3$ GBs is hardly affected by the defects and impurities. It is known that $\Sigma 3$ boundaries are originally electrically inactive [7], and then it is not surprising that they are not so sensitive to passivation.

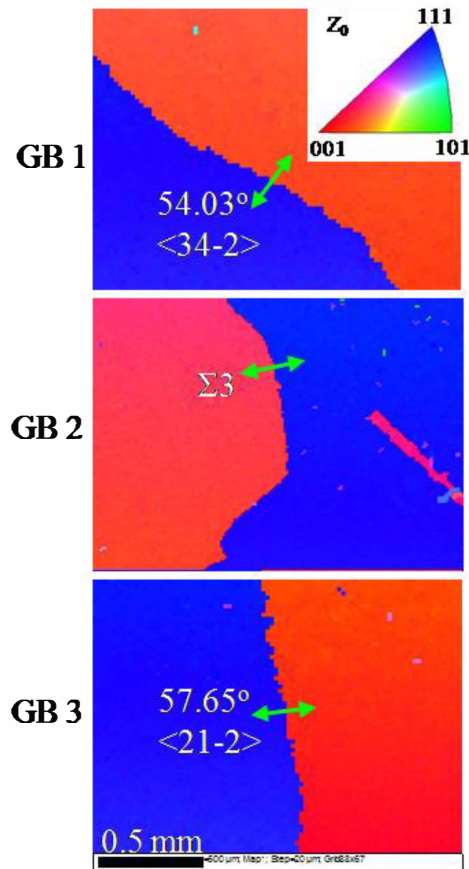


Fig. 3. Plan-view EBSD maps of GB 1, 2, 3. The maps are color-coded with the IPF coloring in the sample normal direction Z_0 . The inset is the color-coding legend.

TABLE I
SHEET RESISTIVITY OF GBs 1–3 UNDER DARK CONDITION

Passivation time (h)		0	5	10	15	20	30
	GB 1	6040.8	5440.5	1277.5	529.1	611.6	503.7
R_{sheet} (Ω/□)	GB 2	138.2	197.5	169.4	135.4	146.8	168.3
	GB 3	3060.7	2826.7	593.4	256.6	255.9	400.9

IV. CONCLUSIONS

In summary, four-point probe, and EBSD techniques were employed to study the passivation effect of three kinds of small polar molecules (methanol, acetonitrile, and formic acid) and our ZK series polar molecule solutions on GBs of mc-Si wafers. It indicates that the latter has much stronger passivation effect than any single type of polar molecules studied. In particular, it is significant that through a 30-hr treatment with ZK-22, the dark R_{sheet} and illuminated R_{sheet} both can be reduced by more than one order for large-angle random GBs. In addition, we found that there is a strong relation between the grain misorientation and the passivation effectiveness. Right polar molecules can passivate random GBs very effectively, but little on $\Sigma 3$ GBs.

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