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# Effect of a silicon nitride film on the potential-induced degradation of n-type front-emitter crystalline silicon photovoltaic modules

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We investigate the effect of silicon nitride ( $\text{SiN}_x$ ) films in n-type front-emitter (n-FE) crystalline Si (c-Si) solar cells on the potential-induced degradation (PID) of n-FE photovoltaic (PV) modules. A negative-bias PID test for a few min does not degrade the performance of PV modules with n-FE cells without  $\text{SiN}_x$ /silicon dioxide ( $\text{SiO}_2$ ) stacks, unlike in the case of PV modules with cells with  $\text{SiN}_x$ / $\text{SiO}_2$ . This is because of the absence of polarization-type PID. After a longer PID test, the PV modules with n-FE cells without  $\text{SiN}_x$ / $\text{SiO}_2$  show a slower decrease in fill factor (FF), originating from Na introduction into the depletion layer of a p–n junction, than the modules with cells with  $\text{SiN}_x$ / $\text{SiO}_2$ .

The mitigation of PID by eliminating  $\text{SiN}_x$  is partly consistent with the results of PV modules with p-type conventional cells without  $\text{SiN}_x$  in which no PID occurs.  $\text{SiN}_x$  thus has a function of enhancing Na introduction into c-Si.

## 1. Introduction

In recent years, large-scale photovoltaic (PV) power plants have been constructed all over the world. Such large-scale PV power plants generally have a high system voltage of 1000 V or more, leading to the smaller number of system components and a reduction in the cost of electricity. This high voltage, however, can cause a performance loss of PV modules referred to as potential-induced degradation (PID).<sup>1-4)</sup> PID is a phenomenon in which the performance of PV modules degrades due to a potential difference between an aluminum (Al) frame and cells. PID has been recognized as one of the most important reliability issues for PV modules, because it can take place in a short duration — from a few months to a few years. The behaviors and mechanisms of the PID of PV modules are known to be different depending of the structure of cells in the modules.

n-type crystalline silicon (c-Si) solar cells generally have higher conversion efficiency than p-type ones, because holes, minority carriers in n-type c-Si, have a smaller capture cross section for many impurities than electrons, minority carriers in p-type c-Si.<sup>5,6)</sup> In addition, p-type c-Si cells can suffer from light-induced degradation due to the formation of the boron (B)–oxygen (O) complexes, which increases the recombination rate of minority carriers.<sup>7,8)</sup> For these reasons, PV modules consisting of n-type c-Si solar cells are expected to have more share in the PV market in the near future.<sup>6)</sup> On the other hand, unlike in the case of the PV modules with p-type c-Si solar cells,<sup>1-4, 9-15)</sup> for which much research on PID has been conducted, there is less sufficient knowledge about the PID of the PV modules consisting of n-type c-Si cells.<sup>16-31)</sup> It is therefore necessary to perform more detailed research on PID for the n-type c-Si PV modules.

n-type front-emitter (n-FE) c-Si PV modules have been reported to exhibit three-stage degradations.<sup>28-30)</sup> In this paper, we refer to these degradations as PID-1, PID-2, and

PID-3, in the order corresponding to their emergences. PID-1 is characterized by simultaneous decreases in short-circuit current density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ), due to the enhancement of surface recombination by the accumulation of positive charges in a front-side Si nitride ( $\text{SiN}_x$ ) antireflection film. We have proposed that the origin of the positive charges is positively-charged K centers in  $\text{SiN}_x$ , dangling bonds backbonded to three nitrogen atoms.<sup>26,29)</sup> PID-2 is characterized by a decrease in fill factor (FF). This degradation may be caused by the introduction of sodium (Na) atoms into the depletion layer of the p–n junction through the  $\text{SiN}_x$  and/or from cell edges.<sup>28)</sup> PID-3 is characterized by additional reductions in  $V_{oc}$  and FF, triggered by further introduction of Na and resulting formation of Na-based dome-like protrusions composed mainly of Na on the top of pyramids on the cell surface.<sup>30)</sup>

Although the behaviors and mechanisms of the PID of n-FE PV modules have been clarified to some extent, they can be influenced by the structure of the cells, which is important to understand the degradation mechanisms in more detail and to establish measures for the suppression of the PID. For example, PV modules with n-FE cells without  $\text{SiO}_2$  between  $\text{SiN}_x$  and c-Si do not exhibit PID-1, whereas they show more rapid and serious PID-2 and PID-3 than the modules with the cells with  $\text{SiO}_2$ .<sup>31)</sup> These results indicate that  $\text{SiO}_2$  acts as a barrier to prevent the charge exchange between  $\text{SiN}_x$  and c-Si and delays the introduction of Na into c-Si in the PID of n-FE modules.

The surface  $\text{SiN}_x$  may also affect the PID of n-FE PV modules. Surprisingly and interestingly, it has been reported that PID does not occur in PV modules with p-type cells from which  $\text{SiN}_x$  is removed.<sup>15)</sup> The similar effect can be seen in PID-2 and PID-3 of n-FE PV modules, since the PID of conventional p-type c-Si PV modules also originates from Na introduction into c-Si. In this study, we investigate the PID of n-FE PV modules

with n-FE cells without SiN<sub>x</sub> and clarify how the PID behaviors are different from the modules with n-FE cells with SiN<sub>x</sub>. The results also give us valuable knowledge for the commonalities and differences between the PID of the PV modules with p-type and n-type cells.

## 2. Experiment methods

We used commercial n-type bifacial cells with SiN<sub>x</sub>/SiO<sub>2</sub> stacks on both sides, from which the SiN<sub>x</sub>/SiO<sub>2</sub> stack on the p<sup>+</sup> emitter side was removed. The cells originally had a size of 156×156 mm<sup>2</sup>, which were cleaved to a few centimeter small pieces. As the first step for the removal of SiN<sub>x</sub>/SiO<sub>2</sub>, 1-methoxy-2-propyl acetate (photoresist solution) was coated on the n<sup>+</sup> layer side of the cells as a protective film. The SiN<sub>x</sub>/SiO<sub>2</sub> stack on the p<sup>+</sup> layer side was then removed using 55% hydrofluoric acid (HF) solution. Ag electrodes on the p<sup>+</sup> emitter side were also removed during this process. The coated photoresist films were removed in acetone after the removal of SiN<sub>x</sub>/SiO<sub>2</sub>. Since it is difficult to completely remove the photoresist, a slight amount of the photoresist remains on the back side of the cells. Ag electrodes were then formed by evaporation through a hard mask. Part of the back-side SiN<sub>x</sub>/SiO<sub>2</sub> was unintentionally etched off during the HF treatment, due to imperfect protection by the photoresist. The cells were thus finally cleaved to a small size so that the cells do not contain the remaining photoresist and the back-side of the cells are fully covered with SiN<sub>x</sub>/SiO<sub>2</sub>. We also used normal n-FE cells from which SiN<sub>x</sub>/SiO<sub>2</sub> was not removed for comparison.

We then fabricated PV modules composed of conventional cover glass/ethylene vinyl acetate copolymer (EVA)/cell/EVA/polyvinyl fluoride (PVF)/polyethylene terephthalate (PET)/PVF backsheets. One module contained only one n-FE cell, and the

area of the modules was  $45 \times 45 \text{ mm}^2$ . The PV modules received a PID test based on the Al-plate method.<sup>32)</sup> PID tests were performed on the modules by applying a negative bias of  $-1000 \text{ V}$  to shorted interconnector ribbons of the modules with respect to a grounded Al plate placed on the cover glass surface using TOS7210S (Kikusui Electronics Corp.) at a temperature of  $85 \text{ }^\circ\text{C}$  and a relative humidity of  $<2\%$ .

To evaluate the degradation of the PV modules, we performed dark and one-sun-illuminated current density–voltage ( $J$ – $V$ ), and external quantum efficiency (EQE) measurements on the PV modules before and after the PID tests. The measured dark  $J$ – $V$  data before and after the PID tests were analyzed using the two-diode model<sup>33)</sup> to obtain the saturation current densities of the first ( $J_{01}$ ) and second ( $J_{02}$ ) diodes, respectively, the ideality factor of the second diodes ( $n_2$ ), the shunt resistance ( $R_{\text{sh}}$ ), and the series resistance ( $R_s$ ). In this study, the ideality factor of the first diode was fixed to  $n_1=1$ . In order to confirm the initial condition of the cells, electroluminescence (EL) observation was also performed using PVX100 (ITES Co., Ltd.).

### 3. Results

Fig. 1 shows the initial one-sun-illuminated  $J$ – $V$  characteristics of the PV modules with n-FE cells with and without  $\text{SiN}_x/\text{SiO}_2$ . The PV module with the n-FE cell without  $\text{SiN}_x/\text{SiO}_2$  shows smaller  $J_{\text{sc}}$  and  $V_{\text{oc}}$  than the module with the cell with  $\text{SiN}_x/\text{SiO}_2$ . This result is quite reasonable because the films functioning as anti-reflection and surface passivation are missing. Nevertheless, the n-FE modules with n-FE cells without  $\text{SiN}_x/\text{SiO}_2$  can be utilized for the PID experiment, because severe decreases in FF due to changes in  $R_{\text{sh}}$  and  $R_s$  are not seen. This also indicates that the evaporated Ag electrodes have a sufficiently low contact resistance with a bare  $\text{p}^+$  emitter. The EL image of the

module with the n-FE cell without  $\text{SiN}_x/\text{SiO}_2$  is shown in the inset of Fig. 1. One can see no cracks or defects which can be formed during the  $\text{SiN}_x$  removal and module fabrication processes.

Fig. 2 shows the normalized  $J_{sc}$ ,  $V_{oc}$ , FF, and maximum output power ( $P_{max}$ ) of the modules with n-FE cells with and without  $\text{SiN}_x/\text{SiO}_2$  as a function of PID-stress duration. We see no PID-1, characterized by decreases in  $J_{sc}$  and  $V_{oc}$  due to positive charge accumulation in  $\text{SiN}_x$ , in the modules with cells without  $\text{SiN}_x/\text{SiO}_2$ . This is reasonable because of the absence of  $\text{SiN}_x$  serving as a charge storage layer and of  $\text{SiO}_2$  having the function of barriers for charge exchange.<sup>31)</sup> PID-2, characterized by a decrease in FF alone due to Na introduction into the depletion layer of the p–n junction and resulting carrier recombination there, is seen in the modules with cells without  $\text{SiN}_x/\text{SiO}_2$  in a longer-duration PID test, like in the case of the modules with cells with  $\text{SiN}_x/\text{SiO}_2$ . Note that the emergence of the FF reduction is delayed in the modules with cells without  $\text{SiN}_x/\text{SiO}_2$  compared to the modules with cells with  $\text{SiN}_x/\text{SiO}_2$ . FF values continue to decrease with increase in the PID-stress duration in both types of modules, and are then saturated. The saturated FF is almost constant independent of the presence or absence of  $\text{SiN}_x/\text{SiO}_2$  in the cells. Further increase in the PID-stress duration results in an increase in FF. The reason for the increase in FF is unclear at present. One possible explanation is that Na-based dome-like structures start to be formed on the surface of the cells and Na in a depletion region is sucked out into the Na domes.<sup>30)</sup> The formation of the dome-like structures can induce further decreases in  $V_{oc}$  and FF due to the destruction of  $\text{SiN}_x$  and p-n junction — PID-3 in this paper.<sup>30)</sup> Although PID-3 is seen in the modules with n-FE cells with  $\text{SiN}_x/\text{SiO}_2$ , the modules with cells without  $\text{SiN}_x/\text{SiO}_2$  show almost no further  $V_{oc}$  and FF reductions even after a significantly long-duration (>100 h) PID test. This is



also a clear indication of the delay of Na-related PID by the removal of  $\text{SiN}_x$ . Note that, although  $\text{SiO}_2$  is also removed in this experiment, the removal of  $\text{SiO}_2$  is not the reason for the delays of PID-2 and PID-3, because we have previously confirmed that the modules with n-FE cells with  $\text{SiN}_x$  alone show rather acceleration of Na-derived PID.<sup>31)</sup>

Fig. 3 shows the dark  $J$ - $V$  curves of the n-FE c-Si PV module with a cell without  $\text{SiN}_x/\text{SiO}_2$  before and after the PID test. Fig. 4 shows the results of two-diode fitting for the dark  $J$ - $V$  curves shown in Fig. 3. Increases in  $n_2$  and  $J_{02}$  are seen at a PID-test duration for 3–6 h. This corresponds to the emergence and progression of the decrease in FF shown in Fig. 2. These tendencies are similar to the results of our previous work,<sup>28)</sup> whereas the onset of the increases in  $n_2$  and  $J_{02}$  is delayed. Note that, although  $R_{\text{sh}}$  obtained by the two-diode fitting decreases, no noticeable shunting is confirmed near the origin of the dark  $J$ - $V$  characteristics, as shown in the inset of Fig. 3(b). We therefore consider that the main reason for the decreases in FF and  $R_{\text{sh}}$  is not the formation of shunting path but the enhancement of recombination current.

#### 4. Discussion

As described above, PID-2 is associated with the introduction of Na into the depletion layer of the p–n junction. Hence, the fact that the removal of  $\text{SiN}_x$  from n-FE cells leads to the delay of PID-2 means that  $\text{SiN}_x$  has a function of accelerating Na-derived PID. This is partially consistent with the previous result about the PID of modules with p-type c-Si cells without  $\text{SiN}_x$ , in which their PID is completely suppressed.<sup>15)</sup> It is seemingly mysterious that the removal of  $\text{SiN}_x$ , known as a good diffusion barrier against Na ions,<sup>34)</sup> leads to the mitigation of Na-derived PID. Although Na ions can drift through  $\text{SiN}_x$  with the assistance of a strong electric field,<sup>35)</sup> the voltage drop in  $\text{SiN}_x$  results in a

smaller electric field in glass and encapsulant (EVA). Hence, the Si surface of the n-FE cells without  $\text{SiN}_x/\text{SiO}_2$  must receive more Na ions than that of the cells with  $\text{SiN}_x/\text{SiO}_2$  in the same PID-test duration, which conflicts the obtained experimental results. The removal of  $\text{SiN}_x$  thus rather affects the process of Na introduction into c-Si, and  $\text{SiN}_x$  may act to squeeze Na into Si. Since the diffusion coefficient of Na in Si at temperatures of  $<100\text{ }^\circ\text{C}$  is quite small,<sup>36)</sup> Na atoms cannot invade c-Si through the simple diffusion process, and an effective driving force for the introduction of Na into Si must be provided from  $\text{SiN}_x$ . One possible mechanism for the Na introduction into c-Si is the assist of positive charges in  $\text{SiN}_x$ .  $\text{SiN}_x$  generally has positive charges if it is on c-Si, and positively-charged Na ions can be repelled and pushed into c-Si. The second possible effect of  $\text{SiN}_x$  is the strong accumulation of Na between  $\text{SiN}_x$  and c-Si. As described above,  $\text{SiN}_x$  has a high barrier property against Na, and the Na ions that have penetrated through the  $\text{SiN}_x$  must be highly localized underneath the  $\text{SiN}_x$ . The heavy accumulation of Na at a  $\text{SiN}_x/\text{c-Si}$  interface has been actually observed in p-type c-Si cells.<sup>12)</sup> The heavy accumulation of Na might be related to the introduction of Na into c-Si. In the case of the cells without  $\text{SiN}_x$ , Na ions may be concentrated less heavily in the vicinity of the c-Si surface, which might mitigate the invasion of Na into c-Si. The third possible mechanism is the influence of  $\text{SiN}_x$  on the formation of Na-decorated stacking faults (SFs).<sup>12,13)</sup> Naumann et al. have experimentally confirmed the introduction of Na into c-Si through the formation of Na-decorated SFs. The formation of Na-decorated SFs might be triggered by  $\text{SiN}_x$ , and the properties of  $\text{SiN}_x$ , such as stress, density, and thickness, perhaps influence the formation of Na-decorated SFs. Actually, the PID of PV modules with conventional p-type cells can be suppressed by the usage of modified  $\text{SiN}_x$ .<sup>37)</sup> If this hypothesis is true, Na atoms on the cell without  $\text{SiN}_x$  are completely free from the trigger for the formation of Na-decorated

SFs, and Na introduction into c-Si can be suppressed. Further detailed work is needed for the clarification of the mechanism for the mitigation of Na-derived PID by the removal of SiN<sub>x</sub>.

Another interesting fact in the PID of PV modules with cells without SiN<sub>x</sub> is the difference of PID behaviors between p-type cells and n-type cells. The modules with p-type cells without SiN<sub>x</sub> show no degradation at all,<sup>15)</sup> whereas the modules with n-FE cells without SiN<sub>x</sub> show an FF reduction induced by Na introduction after a sufficiently long PID test. This difference may originate from the polarity of the emitter into which Na is introduced. As mentioned above, Na introduction into c-Si is believed to proceed through the formation of Na-decorated SFs.<sup>12,13)</sup> Na-decorated SFs are more stable in p-type c-Si than in n-type c-Si.<sup>38)</sup> Based on these facts, Na introduction into p-type c-Si, the emitter for n-FE cells, can proceed more preferentially than Na introduction into n-type c-Si, the emitter for p-type cells, and Na ions are introduced into c-Si to some extent even without the help of SiN<sub>x</sub> only in the case of n-FE modules.

In reality, the removal of SiN<sub>x</sub> from n-FE cells cannot be measures for the suppression of PID because of the poor initial characteristics of the cells without SiN<sub>x</sub>. However, further investigations on the mechanism of Na introduction into c-Si will lead to the establishment of ways for preventing Na introduction into c-Si and resulting Na-derived PID by, e.g., interface engineering and/or the control of SiN<sub>x</sub> properties.

## 5. Conclusion

We have investigated the effect of SiN<sub>x</sub> on the PID of n-FE c-Si PV modules. The removal of SiN<sub>x</sub> from n-FE cells results in the disappearance of PID-1, characterized by reductions in  $J_{sc}$  and  $V_{oc}$  due to positive charge accumulation, which is reasonable because

the positive charges are stored in  $\text{SiN}_x$ . PID-2, an FF reduction due to the introduction of Na into Si, and PID-3, reductions in FF and  $V_{oc}$  by the formation of Na-based dome-like structures, are delayed and mitigated by the usage of n-FE cells without  $\text{SiN}_x/\text{SiO}_2$  in PV modules. Also considering the fact that the PID of p-type c-Si PV modules with cells without  $\text{SiN}_x$  is completely suppressed,  $\text{SiN}_x$  has a function of introducing Na ions into c-Si. The incomplete suppression of Na-derived PID in n-FE PV modules by the removal of  $\text{SiN}_x$  may be due to the difference of the polarity of the emitter layer,  $n^+$  c-Si in p-type cells and  $p^+$  c-Si in n-FE cells, into which Na is introduced.

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## Figure captions

Fig. 1 Initial one-sun-illuminated  $J$ - $V$  characteristics of PV modules with n-FE cells with and without  $\text{SiN}_x/\text{SiO}_2$ . The EL image of the module with a cell without  $\text{SiN}_x/\text{SiO}_2$  is also shown in the inset.

Fig. 2  $J_{sc}$ ,  $V_{oc}$ , FF, and  $P_{max}$ , normalized by their initial values, of the n-type FE c-Si PV modules with cells with and without  $\text{SiN}_x/\text{SiO}_2$  as a function of PID-stress duration. Each data point shows the mean value for three modules, and each error bar corresponds to the standard deviation of the mean.

Fig. 3 Dark  $J$ - $V$  characteristic of the n-FE c-Si PV module with a cell without  $\text{SiN}_x/\text{SiO}_2$  before and after the PID test plotted in (a) log scale and (b) linear scale.

Fig. 4  $J_{01}$ ,  $J_{02}$ ,  $R_{sh}$ , and  $n_2$  of the n-FE c-Si PV module with a cell without  $\text{SiN}_x/\text{SiO}_2$  obtained from dark  $J$ - $V$  characteristics as a function of PID-stress duration.

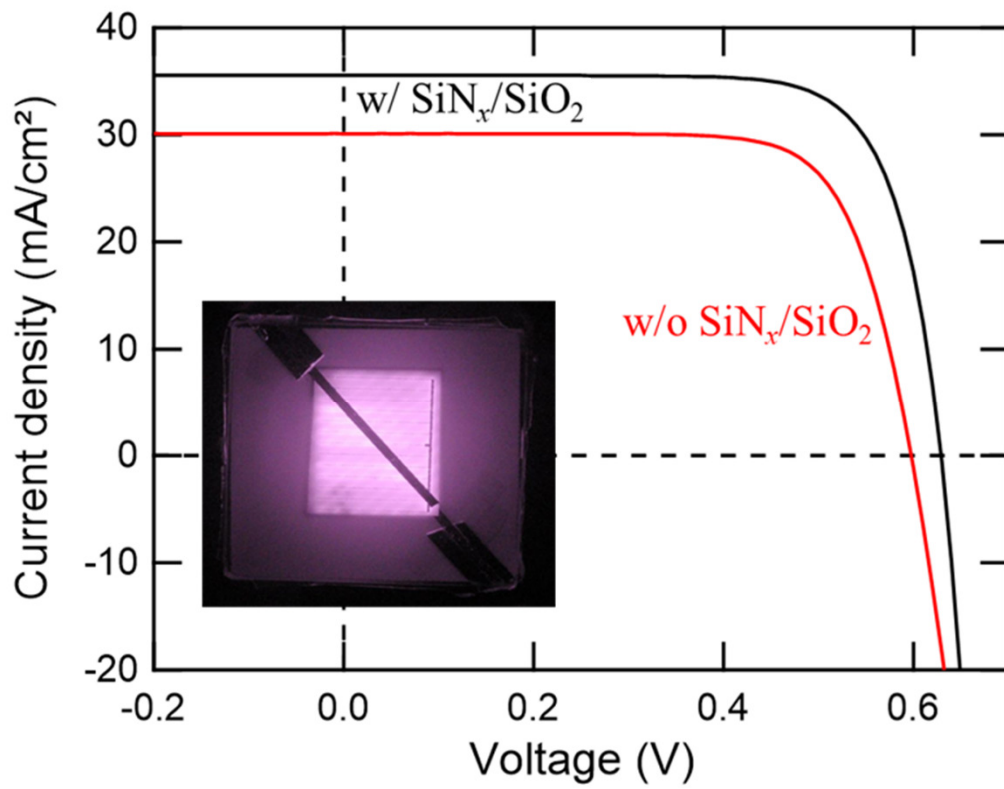


Fig. 1. (Color online) T. Suzuki et al.,

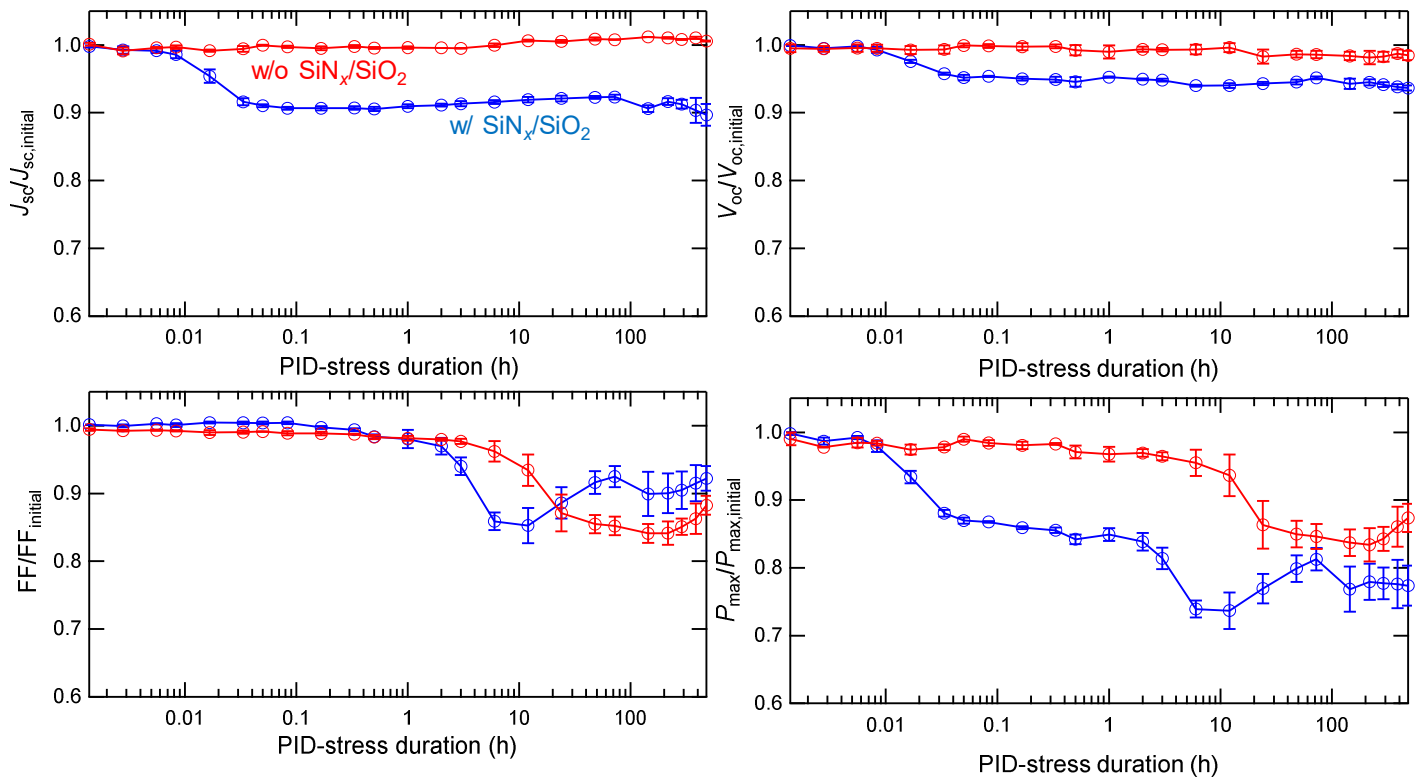


Fig. 2. (Color online) T. Suzuki et al.,

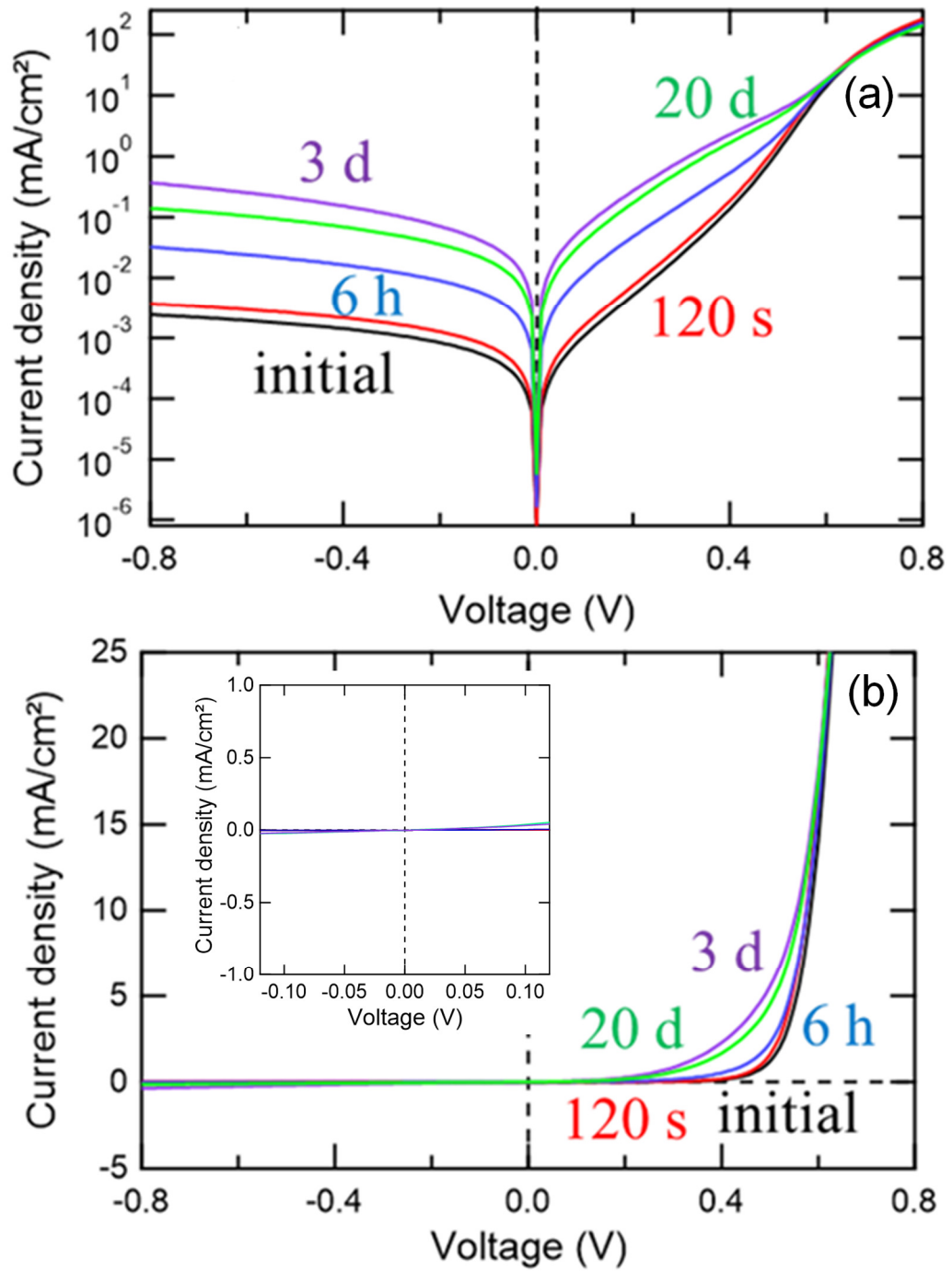


Fig. 3. (Color online) T. Suzuki et al.,

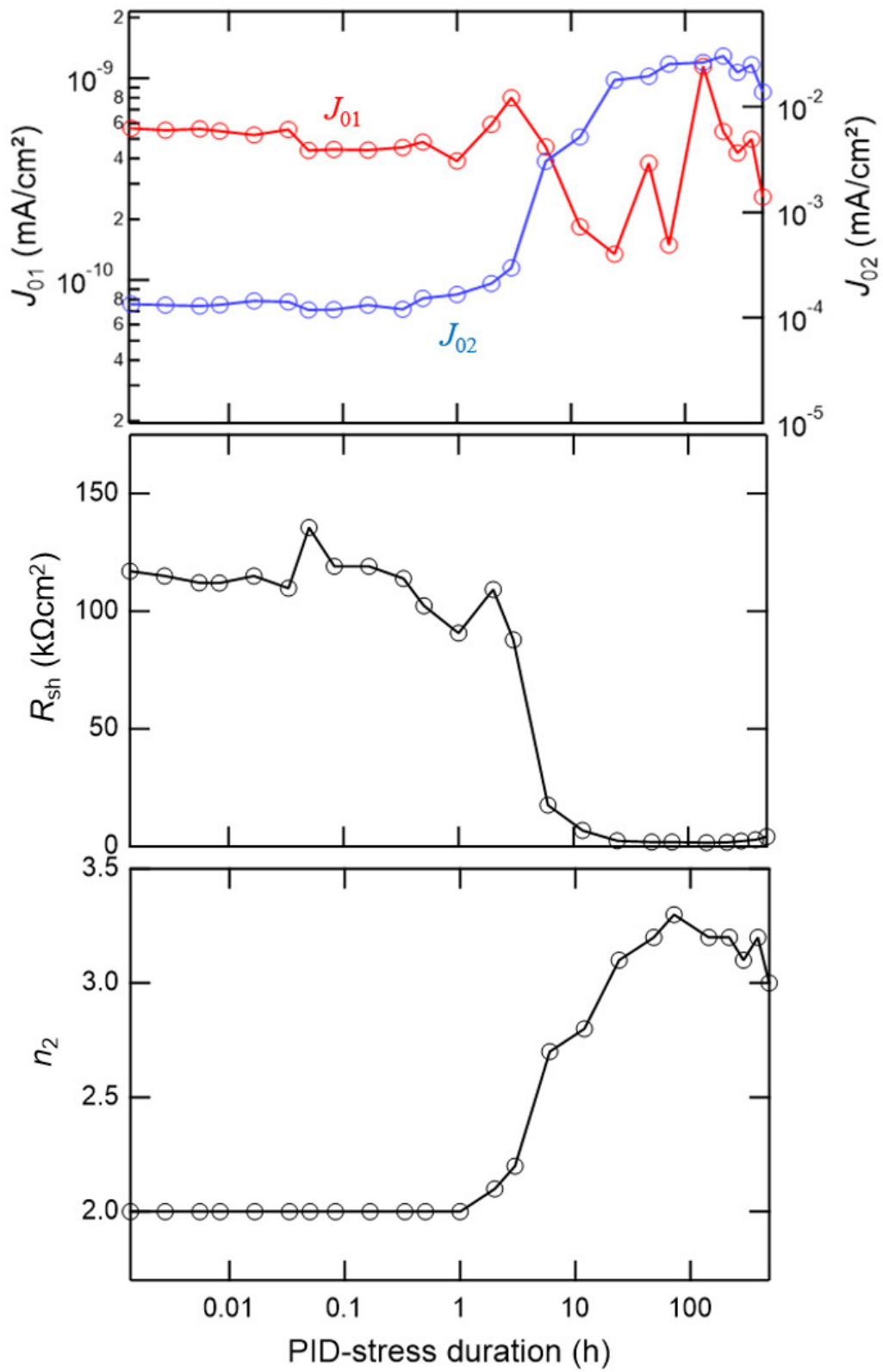


Fig. 4. (Color online) T. Suzuki et al.,