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Abstract

Variation in the formation energy of stacking faults (SFs) with the contamination of sodium atoms was examined in silicon crystals with different Fermi levels. Sodium atoms would agglomerate at SFs under an electronic interaction, leading to a reduction in the SF formation energy. The energy decreased with falling the Fermi level: it was reduced by more than 10 mJ/m^2 in p-type silicon while it was barely reduced in n-type silicon. Due to the energy reduction, Na atoms agglomerating at SFs in p-type silicon would be stable in comparison with in n-type silicon, and this hypothesis was supported by *ab-initio* calculations.

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Photovoltaic (PV) power plants, based on sustainable and cost-competitive technologies, are widely recognized as a clean energy source that contributes to reducing global environmental problems involving CO_2 emission. They are expected to provide a PV energy of 4.7 TW by 2050 [1], which will correspond to a 16% share in the global electricity mix. The reliability of PV technologies, as well as the improvement of the PV efficiency and the reduction of manufacturing cost, have therefore caught attention towards the future-oriented development.

In megawatt-scale PV power plants, a number of PV modules, a majority of which are fabricated with p-type silicon (Si) solar cells, [2, 3] are connected in series so as to generate high voltages and power. High-voltage stresses, up to several hundreds of volts, are inevitably applied between each cell and its module frame. As reviewed by Luo, *et al.* [4], these stresses can lead to a catastrophic power drop in the module (a so called potential induced degradation (PID)) [5]. The PID mechanism in p-type Si solar cells has been aggressively studied, and it is shown that the key factor of the PID is sodium (Na) atoms existing inside [6-9] and on [10] solar module encapsulation (such as cover glass and SiN_x antireflection coating layer), as well as on Si cells [11]. During operation, these Na atoms accumulate at the SiN_x/Si interface, and agglomerate at stacking faults (SFs) in Si cells expanding from the interface [6]. Na atoms prefer to locate onto a SF [12, 13], creating a conductive layer [12]. This can provide a high conductivity between n-doped emitter and p-doped base when the SF penetrates the n-p junction, resulting in a reduction of the shunt resistance which degrades the solar cell performance [6]. Indeed, the PID power loss correlates with the amount of Na atoms [14]. Due to a PID stress under the influence of Na penetration, these SFs would nucleate from microscopic defects at the interface [15], such as dislocations [16], and they would grow via the diffusion of Na atoms in the SFs decorated with Na atoms [12], which is much faster in comparison with in bulk Si [17]. The Na penetration processes would be modified depending on the doping level in Si cells [18]. Also, the amount of Na atoms agglomerating at SFs in p-type Si seems to be larger in comparison with in n-type Si [19]. These results suggest that the formation energy of SFs depends on the Fermi level, as well as on the existence of Na atoms. In this work, we have examined the interaction of Na atoms with SFs in Si crystals with different Fermi levels, leading to a reduction in the SF formation energy. An electronic interaction of Na atoms with SFs depending on the Fermi level was determined by transmission electron microscopy (TEM) and first principles calculations based on density functional theory. Our microscopic finding would provide a guidance to design PID-resistant Si solar cells.

Specimens were dislocation-free Si single crystals grown by the Czochralski method: p-type Si (doped with boron (B) atoms with a carrier concentration $c = 8 \times 10^{18}$ cm^{-3}), n-type Si (doped with phosphorus (P) atoms with $c = 3 \times 10^{19}$ cm^{-3}), and nominally undoped n-type Si ($c = 3 \times 10^{13}$ cm^{-3}) [20]. SF ribbons bound by pairs of partial dislocations (in a density about 10^9 cm^{-2}) were intentionally introduced into the crystals by applying a compressive stress in an argon (Ar) gas atmosphere at an elevated temperature of 1173 K for 0.5 h [20]. Each crystal and a Na sample (Nippon Soda, purity; 99.95%) were sealed within a stainless steel tube with Ar gas, and the crystal was contaminated with Na atoms by heating the tube in a furnace at 973 K for 5 h [21]. The width of each SF ribbon w_{SF} was estimated by dark-field (DF-) TEM [22], as a function of the line orientation α defined as the angle of **b** to **u** in which **b** is the sum of the Burgers vectors of the dislocations bounding the SF ribbon and **u** is a vector parallel to the dislocations. The apparent energy for the formation of SFs E_{SF} was then calculated with $w_{SF}(\alpha)$, by using an anisotropic elasticity theory taking into account the deviation parameter [23].

The stability of Na defects at different Fermi levels was examined by density functional theory calculations. We constructed a supercell with a SF consisting of 224 Si atoms, whose cell volume was $1.33 \times 4.40 \times 0.77$ nm^3, and introduced 1 Na interstitial defect to the supercell. In addition to neutral defects (Na(0)), positively charged defects (Na(+)) and negatively charged ones (Na(-)) were considered by either subtracting or adding one electron. We used the projector augmented wave (PAW) method implemented in the VASP code [24-26]. Plane waves with an energy cutoff of 500 eV were used to expand wave functions. The exchange-correlation energy was calculated using a revised version of the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBEsol) [27]. A Γ-centered k-point mesh of $1 \times 2 \times 4$ was used for integration of Brillouin zone. The electrons of $3s^2 3p^2$ for Si and $3s^1$ for Na were treated as valence electrons. Atomic positions were optimized until a force on each atom was smaller than 0.01 eV/A.

Before the contamination with Na impurities, $w_{SF}(\alpha)$ distributed in the range of 4 to 8 nm; it was maximum for $\alpha \sim 90°$ and it was minimum for $\alpha \sim 0°$, owing to the balance between the SF energy and the elastic energy due to partial dislocations [23]. The average of $w_{SF}(\alpha)$ at α increased in Si crystals contaminated with Na atoms. Figures 1(a) to 1(b) show the typical variation observed in p-type Si crystals. The ratio of $w_{SF}(\alpha)$ before and after Na contamination was almost independent of α (Fig. 1(c)). Accordingly, as shown in Fig. 1(d), E_{SF} estimated with the $w_{SF}(\alpha)$ decreased by a constant rate
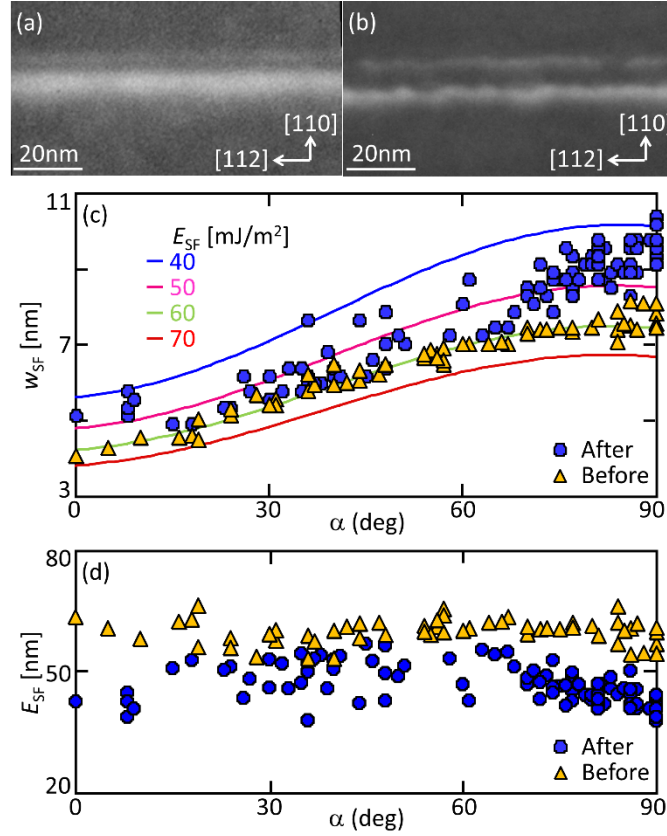
irrespective of α.

Fig. 1 DF-TEM images of a SF with α ~ 90° in p-type Si viewed along the SF normal (with 200 keV electrons with **g** = 220 under the **g**/4**g** condition); (a) before and (b) after the contamination with Na atoms. (c) SF width $w_{SF}(\alpha)$ and (d) SF formation energy E_{SF} before (triangles) and after (circles) Na contamination.

A SF ribbon can widen due to the reduction of the electronic energy via the agglomeration of impurities at the ribbon [20]. Also, impurity atoms can agglomerate at the pair of partial dislocations binding the SF ribbon, so as to reduce the electronic and elastic energies, and this energy reduction would result in the variation in $w_{SF}(\alpha)$. However, although the ability of impurity agglomeration at dislocations, related to the electronic structure and the elastic strains around the dislocation core, would depend on α, Fig. 1(d) shows that E_{SF} is independent of α. Effects of Na agglomeration at partial dislocations are, therefore, negligible in the present experiments. Besides, a Coulomb repulsion in a pair of partial dislocations [28], charged negatively via the displacement

of the Fermi level by Na donors (Patel effect) [29], would be ignored in p-type Si crystals heavily doped with B atoms. These results indicate that Na atoms would agglomerate at SFs due to an electronic interaction, and this interaction results in the reduction of E_{SF}.

Figure 2 shows the energy reduction in E_{SF} induced by Na contamination in Si with different Fermi levels. The reduction in p-type Si was more than 10 mJ/m^2: the averaged E_{SF} of 59 mJ/m^2 before Na contamination decreased to 47 mJ/m^2 (Fig. 2(a)). Similarly, E_{SF} in undoped Si was reduced by Na contamination, even though the energy reduction was a few mJ/m^2 (Fig. 2(b)). Meanwhile, E_{SF} was barely reduced in n-type Si [30] (Fig. 2(c)). These results suggest that the energy reduction in E_{SF} by Na contamination would increase with falling the Fermi level. In other words, Na atoms agglomerating at SFs in p-type Si would be stable in comparison with in n-type Si, due to an electronic interaction of Na atoms with SFs.
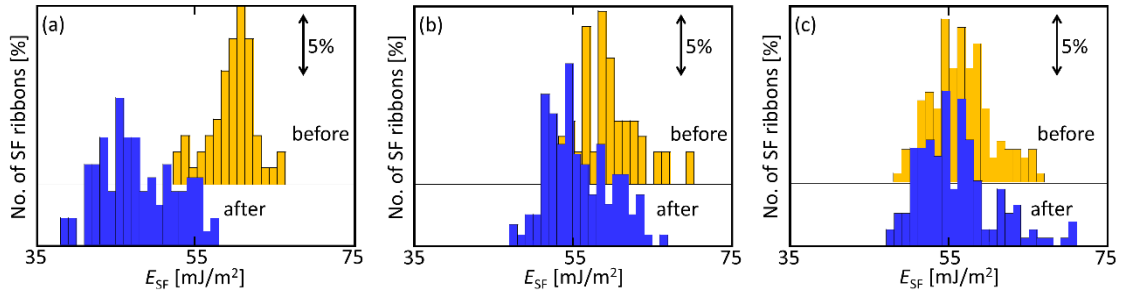

Fig. 2 SF energy E_{SF} before and after Na contamination estimated in (a) p-type, (b) undoped, and (c) n-type Si crystals.

The above-mentioned hypothesis was supported by *ab-initio* calculations. Since no Na precipitate was observed at SFs by TEM, we assumed that isolated Na atoms would agglomerate at SFs. Also, we did not consider Na atoms at substitutional sites, since their formation energy would be rather high [33]. We confirmed that Na atoms are the most stable at the "open sites in SFs" indicated by the square in Fig. 3 while they locate at the tetrahedral sites in Si crystals free from SFs, as previously reported [12]. The binding energy of Na atoms to SFs, E_{bind}, would be determined as the difference between the total energy of the supercell in which the Na atom locates at an "open site in SFs" and that at a tetrahedral site far from the SF, as indicated in Fig. 3. The binding energy was estimated to be 0.7 eV irrespective of the charge state, indicating that the binding energy would be independent of the Fermi level. Besides, the formation energy of Na

defects at the tetrahedral sites free from SFs, E_{TD}, would depend on the Fermi level: the energy in p-type Si would be lower than in undoped and n-type Si [33]. The formation energy of Na defects at the "open sites in SFs", E_{open}, could be approximated to E_{TD} - E_{bind}, and therefore, the energy in p-type Si would be lower than in undoped and n-type Si. Na atoms with a low ionization energy would exist as Na(+) in p-type Si by capturing holes, as expected theoretically [33], and this would result in a low E_{open} in p-type Si. In other words, the interaction of ionized Na atoms with SFs would result in a big reduction of the SF energy in p-type Si.
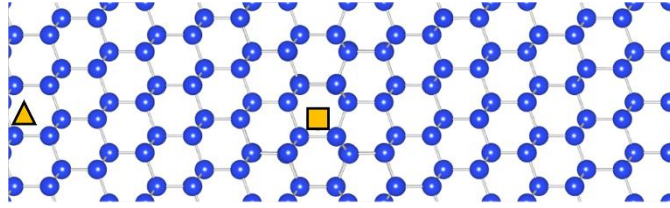

Fig. 3 Supercell of a SF consisting of Si atoms (indicated by circles). The atomic site for interstitial Na indicated by the square and that by the triangle are the "open site in SFs" and the tetrahedral site, respectively, used for our calculations.

Here we discuss the agglomeration process of Na atoms at SFs. It is hypothesized that SFs are formed at the SiN_x/Si interface via the agglomeration of Na atoms, and they expand toward the n-p junction under PID stresses [15]. We have clarified experimentally that the SF formation energy is reduced in Si contaminated with Na atoms, as expected theoretically [12, 13]. Once contaminated SFs are formed, Na atoms can diffuse preferentially along the SFs since the activation energy for Na diffusion in the SFs is lower than that in bulk Si [12]. Under a constant PID stress, the expansion rate of SFs determined by the Na diffusion would increase with increasing the distance from the SiN_x/Si interface, due to the reduction in the SF formation energy depending on the Fermi level (Fig. 2). Especially, it is expected that the expansion rate of SFs would increase rapidly after the SFs penetrate the n-p junction. Such a rapid increase in the expansion rate may result in an abrupt increase in the power loss in solar cells, as reported [5, 14, 16, 34] Indeed, it is speculated that Na diffusion into the n-p junction induces irreversible PID processes [34]. Meanwhile, the expansion rate would decrease with the concentration of n-type dopants, and this may be related to the suppression of the PID in Si heavily doped with P atoms [18] and that in Si cells under photo-

illumination [35]. It is also expected that the amount of Na atoms agglomerating at SFs in p-type Si would be larger than that in n-type Si, as observed in a solar cell after PID [19]. Our results suggest that the PID progression in p-type Si solar cells would depend on the distribution of dopant atoms around the n-p junction, as well as on external factors such as applied voltage and temperature [4].

As reviewed by Luo, *et al*. [4], the PID in p-type Si solar cells can be recovered by annealing and/or by applying a reverse potential, and the recovery process is dependent on the PID history in the cells. It is hypothesized that the process is controlled by out-diffusion of Na atoms from SFs [8]. Due to the out-diffusion, SFs decorated with Na atoms would convert into undecorated SFs, which are electrically inactive [8]. Some p-type Si solar cells exhibit incomplete recovery, probably due to residual Na atoms in SFs [34, 36]. Actually, a SF decorated with Na atoms is observed in a recovered solar cell [37]. These complicated behavior of Na atoms may correlate with the formation energy of the SFs decorated with Na atoms, which is dependent on the Fermi level (Fig. 2). The energy nearby the SiN_x/Si interface, where the concentration of n-type dopants is high, is comparable to the formation energy of SFs without Na atoms. In other words, the interaction of Na atoms with SFs is weak. This weak interaction would assist the out-diffusion of Na atoms nearby the interface. With increasing the distance from the interface, the SF formation energy would decrease, and the stability of Na atoms at SFs would increase. This stability would disturb the out-diffusion of Na atoms in SFs, especially around the n-p junction. Further study to examine the spatial distribution of dopants and Na atoms is necessitous to confirm the model.

In conclusion, the formation energy of SFs decorated with Na atoms was examined in Si crystals with different Fermi levels. The estimated energy decreased with falling the Fermi level: the energy in p-type Si was reduced by more than 10 mJ/m^2 while the energy in n-type Si was comparable to the formation energy of SFs without Na atoms. These results suggest that the PID progression and recovery in p-type Si solar cells, caused via the Na motion in SFs, would correlate with the distribution of dopant atoms around the n-p junction.

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References

[1] IEA, Technology roadmap: solar photovoltaic energy, OECD/IEA, Paris, 2014.

[2] M. Rekinger, F. Thies, G. Masson, and S. Orlandi, Global market outlook for solar power 2015-2019.

[3] F. Colville, Solar cell technology roadmap for 2016.

[4] W. Luo, Y.S. Khoo, P. Hacke, V. Naumann, D. Lausch, S.P. Harvey, J.P. Singh, J. Chai, Y. Wang, A.G. Aberleae, and S. Ramakrishna, Energy Environ. Sci. **10**, 43 (2017).

[5] S. Pingel, O. Frank, M. Winkler, S. Daryan, T. Geipel, H. Hoehne and J. Berghold, Proc. 35th IEEE Photovoltaic Specialists Conf. (2010), pp.2817.

[6] V. Naumann, D. Lausch, A. Hahnel, J. Bauer, O. Breitenstein, A. Graff, M. Werner, S. Swatek, S. Groser, J. Bagdahn, and C. Hagendorf, Sol. Energy Mater. Sol. Cells **120**, 383 (2014).

[7] V. Naumann, C. Hagendorf, S. Grosser, M. Werner, and J. Bagdahn, Energy Proc. **27**, 1 (2012).

[8] D. Lausch, V. Naumann, A. Graff, A. Hahnel, O. Breitenstein, C. Hagendorf, and J. Bagdahn, Energy Proc. **55**, 486 (2014).

[9] J. Bauer, V. Naumann, S. Groser, C. Hagendorf, M. Schutze, and O. Breitenstein, Phys. Status Solidi Rapid Res. Lett. **6**, pp. 331 (2012).

[10] S. Suzuki, N. Nishiyama, S. Yoshino, T. Ujiro, S. Watanabe, T. Doi, A. Masuda, and T. Tanahashi, Jpn. J. Appl. Phys. **54** (2015) 08KG08.

[11] V. Naumann, D. Lausch, and C. Hagendorf, Energy Proc. **77**, 397 (2015).

[12] B. Ziebarth, M. Mrovec, C. Elsesser, and P. Gumbsch, J. Appl. Phys. **116** (2014) 093510.

[13] C. Wang, H. Li, C. Li, G. Wu, T. Sang, L. Yang, Z. Wang, Comput. Mater. Sci. **118**, 16 (2016).

[14] T. Kawamura, Y. S. Khoo, T. Zhao, Y. Wang, and A. G. Aberle, Jpn. J. Appl. Phys. **56**, 122301 (2017).

[15] V. Naumann, C. Brzuska, M. Weaner, S. Grosser, and C. Hagendorf, Energy Proc. **92**, 569 (2016).

[16] X. Gou, X. Li, J. Yu, S. Wang, X. Zhang, S. Zhou, W. Fan, and Q. Huang, Phys. Status Solidi A **214**, 1700006 (2017).

[17] V. M. Korol, Phys. Status Solidi A **110**, 9 (1988).

[18] J. Oh, B. Dauksher, S. Bowden, G. Tamizhmani, P. Hacke, and J. D'Amico, IEEE J.

Photovolt. **7**, 437 (2017).

[19] S. P. Harvey, J. A. Aguiar, P. Hacke, H. Guthrey, S. Johnston, and M. Al-Jassim, IEEE J. Photovolt. **6**, 1440 (2016).

[20] Y. Ohno, T. Taishi, Y. Tokumoto, and I. Yonenaga, J. Appl. Phys. **108**, 073514 (2010).

[21] H. Morito, T. Karahashi, and H. Yamane, J. Cryst. Growth **355**, 109 (2012).

[22] Y. Ohno, T. Shirakawa, T. Taishi, and I. Yonenaga, Appl. Phys. Lett. **95**, 091915 (2009).

[23] D. J. H. Cockayne, I. L. F. Lay, and M. J. Whelan, Philos. Mag. **20**, 1265 (1969).

[24] G. Kresse and J. Furthmuller, Comput. Mater. Sci., **6**, 15 (1996).

[25] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).

[26] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[27] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).

[28] M. Sato, K. Sumino, and K. Hiraga, Phys. Status Solidi A **68**, 567 (1981).

[29] J. R. Patel, L. R. Testardi, and P. E. Freeland, Phys. Rev. B **13**, 3548 (1976).

[30] The SF formation energy E_{SF} in as-grown Si doped with n-type dopant atoms is smaller than that in undoped Si (58-60 mJ/m^2) due to the interaction between the dopant atoms and SFs [20], although the interaction is rather weak as confirmed experimentally [31] and theoretically [32]. For P-doped Si with $c = 3 \times 10^{19}$ cm^{-3}, $E_{SF} \sim 56$ mJ/m^2 [20].

[31] Y. Ohno, K. Inoue, Y. Tokumoto, K. Kutsukake, I. Yonenaga, N. Ebisawa, H. Takamizawa, Y. Shimizu, K. Inoue, Y. Nagai, H. Yoshida, and S. Takeda, Appl. Phys. Lett. **103**, 102102 (2013).

[32] Y. Yamamoto, K. Togase, Y. Ohno, I. Yonenaga, and S. R. Nishitani, Jpn. J. Appl. Phys. **53**, 061302 (2014).

[33] J. S. Park and M. K. Y. Chan, J. Appl. Phys. **123**, 161560 (2018).

[34] A. Masuda, M. Akitomi, M. Inoue, K. Okuwaki, A. Okugawa, K. Ueno, T. Yamazaki, and K. Hara, Curr. Appl. Phys. **16**, 1659 (2016).

[35] P. Hacke, K. Terwilliger, S. Glick, G. Tamizhmani, S. Tatapudi, C. Stark, S. Koch, T. Weber, J. Berghold and S. Hoffmann, IEEE J. Photovolt. **5**, 94 (2015).

[36] J. Oh, S. Bowden, and G. TamizhMani, IEEE J. Photovolt. **5**, 1540 (2015).

[37] V. Naumann, D. Lausch, A. Hahnel, O. Breitenstein, and C. Hagendorf, Phys. Status Solidi C **12**, 1103 (2015).