Minority Carrier Recombination Properties of Crystalline Defect on Silicon Surface Induced by Plasma Enhanced Chemical Vapor Deposition

Tomihisa Tachibana, a, b Daisuke Takai, b Takuto Kojima, b Takefumi Kamioka, b Atsushi Ogura, c and Yoshio Oshita b

a National Institute of Advanced Industrial Science and Technology (AIST), Fukushima Renewable Energy Institute, AIST (FREA), Koriyama 963-0298, Japan
b Toyota Technological Institute, Nagoya 468-8511, Japan
c Meiji University, Kawasaki, Kanagawa 214-8571, Japan

This research investigates the carrier recombination properties of a crystalline defect layer introduced by the plasma enhanced chemical vapor deposition (PECVD) process of amorphous hydrogenated silicon nitride (SiNx) passivation films. A direct PECVD technique was used for SiNx films deposition. A crystalline defect layer existed on the surface of the silicon substrate and is under the SiNx passivation film. The recombination lifetime in this defect layer was obtained by focusing on the thickness of the defect layer and the effective lifetime before and after the defect layer etching. After etching a few nanometer thickness, effective lifetime drastically increased. On the other hands, the carrier recombination center could be electrically inactivated by 600°C annealing after SiNx deposition. According to the depth profile of effective lifetime, it was clarified that the high carrier recombination region was concentrated near the surface of silicon substrate.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0371609jss] All rights reserved.

The future of the crystalline silicon solar cell industry depends on being able to reduce the production cost and increase the conversion efficiency. In order to realize the high conversion efficiency, the carrier lifetime needs to be increased by reducing the number of crystalline defects and/or inactivating the recombination centers in the bulk and on the surface of the silicon substrates. Crystalline defects, such as grain boundaries, dislocations, and impurities, act as recombination centers. Therefore, a lot of studies have been carried out to clarify the crystalline defect properties and to investigate the suppression techniques. 1–4 Surface passivation techniques are used on the surfaces of substrates to inactivate the surface recombination centers or dangling bonds. Many materials have been investigated for use in high quality passivation films. 5–9 Passivation can be achieved by two mechanisms, one is chemical passivation and the other is field-effect passivation. 10–13

Amorphous hydrogenated silicon nitride (SiNx) passivation films are mainly used as surface coating for crystalline silicon solar cells because of their excellent surface passivation properties as well as their anti-reflection effect. SiNx films also act as a source of hydrogen for the carrier lifetime needs to be increased by reducing the number of crystalline defects and/or inactivating the recombination centers in the bulk and on the surface of the silicon substrates. Crystalline defects, such as grain boundaries, dislocations, and impurities, act as recombination centers. Therefore, a lot of studies have been carried out to clarify the crystalline defect properties and to investigate the suppression techniques. 1–4 Surface passivation techniques are used on the surfaces of substrates to inactivate the surface recombination centers or dangling bonds. Many materials have been investigated for use in high quality passivation films. 5–9 Passivation can be achieved by two mechanisms, one is chemical passivation and the other is field-effect passivation. 10–13

Amorphous hydrogenated silicon nitride (SiNx) passivation films are mainly used as surface coating for crystalline silicon solar cells because of their excellent surface passivation properties as well as their anti-reflection effect. SiNx films also act as a source of hydrogen for surface and bulk defects passivation. An annealing process can be used to diffuse the hydrogen contained in these films. 14–16 Plasma-enhanced chemical vapor deposition (PECVD) technique is used to form most of the SiNx passivation films because it allows for the fabrication of SiNx films at a low temperature. 16–18 However, the plasma process causes surface damage as crystalline defects due to the plasma and/or ion bombardment. 18–22 A case of crystalline defects introduced by PECVD is shown in Fig. 1. The crystalline defects exist at the surface of the silicon wafer, especially at the top of the texture structure. There are some reports about the relationship between the passivation properties and surface damage. 23, 24 However, in these reports, the main topics are the passivation properties and not the carrier recombination at the defect layer in the silicon substrate. It is necessary to separate components, such as lifetime degradation by the defect layer and carrier recombination suppression by the passivation.

In this paper, the carrier recombination activity of crystalline defects introduced by PECVD in SiNx passivation films was investigated. The thickness of the crystalline defect layer was observed by transmission electron microscopy (TEM). The depth profile of carrier recombination properties were studied using mirror polished silicon wafers. SiNx passivation properties were determined under several annealing condition.

Experimental

Thickness and carrier recombination properties.—4 inch Czochralski silicon (phosphorus doped n-type, 7–13 Ω cm, double side mirror polished) substrates were used for this study. The wafers were 500 μm thick. A 10:1 diluted hydrogen fluoride (DHF) solution was used to remove the native silicon oxide layer prior to the SiNx passivation films deposition. Then, a direct PECVD technique using monosilane (SiH4) and ammonia (NH3) gasses (SiH4:NH3 = 40:120 sccm) was used to form the SiNx passivation film. The deposition temperature was 450°C, the pressure was 67 Pa, and the radio frequency power was 150 W. SiNx films were deposited on both sides in order to determine the recombination properties. The deposition thickness and refractive index of the SiNx films are approximately 80 nm and 2.1, which were obtained by ellipsometry measurement. After the SiNx film deposition, some samples were annealed by rapid thermal annealing (RTA) from 400 to 600°C in a N2 ambient for 30 sec.

Figure 1. TEM image of texture structure after SiNx deposition.
The effective minority carrier lifetimes were measured using a photo-conductance lifetime tester (Sinton Instruments, WCT-120) operated in transient mode at room temperature. The maximum surface recombination velocity \( S_{\text{max}} \) was estimated from the effective lifetime \( \tau_{\text{eff}} \) by assuming that the bulk lifetime of the silicon substrate is infinity. \( S_{\text{max}} \) was calculated from the following equation,

\[
\frac{1}{\tau_{\text{eff}}} = \frac{2S_{\text{max}}}{W},
\]

where \( W \) is the wafer thickness.

The thickness of the crystalline defect layer was determined by TEM (JEOL JEM-2100) at 200 kV. Electron beam deposition was used to deposit thin carbon films on the SiNx passivation films before the TEM sample preparation in order to protect the SiNx films from ion beam damage on the SiNx films. A focused ion beam (FIB) system was used to prepare the TEM samples, which were approximately 100 nm thick.

For the evaluation of carrier recombination properties in the crystalline defect layer, the SiNx passivation films were removed by DHF. Then, Iodine/Ethanol solution was used to passivate the substrates prior to the effective lifetime measurement. After lifetime measurement, those substrates were cleaned by DHF. Then, the crystalline defect layers were etched with a mixture of NHO3, HF, and CH3COOH at room temperature (NHO3:HIF:CH3COOH = 40:1:15). After etching away a few nanometers, the effective lifetime were measured again. The etching and effective lifetime measurement were done again and again. The etched thicknesses were determined based on the weight difference before and after etching.

**Recombination lifetime calculation.**—The recombination lifetime in the crystalline defect layer was estimated by considering the following. The recombination rate \( U_{\text{total}} \) is expressed as:

\[
U_{\text{total}} = \frac{W \Delta n_{\text{ave}}}{\tau_{\text{eff}}} = \int_{0}^{W} \frac{\Delta n(x)}{\tau_{\text{bulk}}} dx + S_{\text{front}} \Delta n(0) + S_{\text{rear}} \Delta n(W),
\]

where \( W \) is the thickness of silicon substrate, \( S_{\text{front}} \) and \( S_{\text{rear}} \) are the surface recombination velocity \( S \) of the front and rear sides, \( \Delta n_{\text{ave}} \) is the average excess carrier density, \( \Delta n(x) \) is the bulk recombination lifetime. Assuming that \( \Delta n(x) = \text{const.} \) and \( S_{\text{front}} = S_{\text{rear}} = S \), Equation 2 is rewritten as:

\[
\int_{0}^{W} \frac{1}{\tau_{\text{eff}}} dx = \int_{0}^{d} \frac{1}{\tau_{\text{defects layer}}} dx + \int_{d}^{W} \frac{1}{\tau_{\text{bulk}}} dx + 2S,
\]

where \( d \) is the thickness of the crystalline defect layer and \( \tau_{\text{defects layer}} \) is the recombination lifetime in the crystalline defect layer. Additionally, the thickness of the defect layer is thinner than that of the silicon substrate: \( d \ll W \). Thus, the defect layer could be neglected: \( W - 2d \approx W \), and thus, Equation 3 is expressed as:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{2d}{W} \frac{1}{\tau_{\text{defects layer}}} + \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W},
\]

Using Equation 4, \( \tau_{\text{eff}} \) before the etching \( (\tau_{\text{eff-1}}) \) and after the etching \( (\tau_{\text{eff-2}}) \) of the crystalline defect layer can be described as:

\[
\frac{1}{\tau_{\text{eff-1}}} = \frac{2d}{W} \frac{1}{\tau_{\text{defects layer}}} + \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W} \quad \text{and}
\]

\[
\frac{1}{\tau_{\text{eff-2}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W}.
\]

Using Equations 5 and 6, the \( \tau_{\text{defects layer}} \) is assumed to be:

\[
\tau_{\text{defects layer}} = \frac{2d}{W} \left( \frac{1}{\tau_{\text{eff-1}}} - \frac{1}{\tau_{\text{eff-2}}} \right)^{-1}.
\]
corresponds to the bulk lifetime without the damaged layer. This result suggests that the damaged layer act as recombination centers of minority carriers, resulting that the effective lifetime was decreased. On the other hand, in the 600°C annealed substrates without SiNx film, the effective lifetimes were approximately 1400 μsec. This lifetime is almost same as bulk lifetime, although there is damaged layer. Because of 600°C annealing, the defects in the damaged layer were electrically inactivated. The origin of the difference between the effective lifetimes in as-deposition and the 600°C annealed substrates might be hydrogen (H atoms) diffused from SiNx film due to the annealing. Which terminate the defects. From these results, the damaged layer is one of the origin for the difference of effective lifetime in the as-deposition substrates and 600°C annealed substrates. 

For the investigation of the carrier recombination distribution in the damaged layer, the depth profile of recombination properties were evaluated. The recombination at the crystalline defect layer was analyzed using the $S_{\text{max}}$. Since the damaged layer thickness is thin as compared with the wafer thickness, this recombination could be assumed to be the surface recombination. The relationship between $S_{\text{max}}$ and the etched thickness of the crystalline defect layer is shown in Fig. 5. In the as-deposition substrates, $S_{\text{max}}$ was approximately 200 cm/s before etching. It dramatically decreased as increasing the etching layer thickness and becomes to less than half this value after a few nanometer etching. After over 100 nm etching, $S_{\text{max}}$ was saturated approximately 20 cm/sec. This $S_{\text{max}}$ corresponds to the recombination at the passivated surface and bulk. The damaged layer thickness determined by TEM image was around 50 nm. This is thinner than the thickness of the layer which act as recombination centers. On the other hand, $S_{\text{max}}$ obtained from the 600°C annealed wafer was almost same as that without the damaged layer. There is no recombination center which determines the effective lifetime in this substrate.

Considering that $S_{\text{max}}$ drastically decreased after a few nanometer etching in as-deposition substrates, it can be assumed that high density recombination center exist at the near-surface region of the silicon substrates. These results indicate that not the complete crystalline defect layer obtained by TEM acts as carrier recombination center. The carrier recombination centers introduced by plasma damage are concentrated at the near-surface region of the silicon substrates. The origin of the defect layer might be connected to hydrogen and/or nitrogen atoms induced during the PECVD process. The dark contrast in this study is similar to the results found in damage formation promoted by nitrogen atoms during electron beam irradiation.26,27 Nitrogen atoms were introduced into the silicon substrates during PECVD process and the crystalline defect might be formed by electron irradiation. On the other hand, hydrogen atoms could be introduced into the near-surface region of silicon substrates during the plasma process.28,29 Since hydrogen atoms can form high-density carrier recombination centers at the silicon surface, they could explain the carrier recombination properties found in this study. Additionally, the presence of nitrogen could explain the dark TEM contrast.

Recombination lifetime calculation.—We calculated the recombination lifetime in the crystalline defect layer. Using the Equation 7, the thickness of the wafer ($W$) is approximately 500 μm. The crystalline
defect layer thickness \((d)\) is assumed to be approximately 40–50 nm by TEM. \(\frac{1}{\tau_{\text{defect}}} - \frac{1}{\tau_{\text{bulk}}}\) is obtained from the results shown in Fig. 4. Thus, the recombination lifetime in the crystalline defect layer is approximately 20–40 nsec. In case of the crystalline defect layer thickness is thinner than that obtained with TEM, from few nanometer to 10 nm, \(\tau_{\text{defect}}\) decrease to 2–7 nsec.

As a possible explanation for the suppression of surface recombination after passivation, we considered that the defect layer was inactivated by hydrogen diffusion from the SiNx film. Therefore, for fabrication processes that do not include high temperature annealing, the introduction of this defect layer need to be suppressed since no hydrogen diffusion can occur during the fabrication. We reported one technique to suppress the introduction is fabricating the thin oxide layer before PECVD processes. From the view point of system development, technique to do less plasma damage to silicon surface would be required.

**Conclusions**

Carrier recombination properties of the crystalline defect layer introduced by PECVD were investigated using lifetime measurement. The thickness of the defect layer was approximately 40–50 nm as obtained by TEM observation. The carrier recombination properties were obtained using lifetime measurement and nanometer scale etching. Assuming the recombination at the crystalline defect layer is the surface recombination, \(S_{\text{sat}}\) was obtained. In as-deposition substrates, the defect layer acted as a carrier recombination center. After few nanometer defect etching, \(S_{\text{sat}}\) drastically decreased. Therefore, high density recombination centers can be assumed to exist at the near-surface region of the silicon substrates. After the damaged layer was completely removed, the effective lifetime were saturated the value which corresponds to the bulk lifetime without the damaged layer. In 600°C annealed substrates, \(S_{\text{sat}}\) was almost unchanged before and after etching. The defects in the damaged layer were electrically inactivated due to the 600°C annealing. The origin of the crystalline defect might be connected to hydrogen and/or nitrogen atoms induced during the PECVD process. One of the reason for increasing the effective lifetime in 600°C annealed substrates is that the carrier recombination centers at the damaged layer are electrically inactivated.

**Acknowledgments**

This work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of Economy, Trade and Industry (METI). We sincerely thank our co-workers, for their excellent work, and fruitful discussions, and Motoo Morimura, Hiromi Ohniwa, and Mari Aoki for their kind assistance with the experiment.

**References**

1. S. Joonwichten, I. Takahashi, S. Matushima, and N. Usami, *Prog. Photovolt: Res. Appl.*, 22, 726 (2014).
2. K. Kato, N. Usami, Y. Ohno, Y. Tokumoto, and I. Yonenaga, *J-PV*, 4, 84 (2014).
3. G. Kato, M. Tajima, H. Toyoda, and A. Oгуra, *Jpn. J. Appl. Phys.*, 53, 080303 (2014).
4. T. Tachibana, K. Sato, H. Kusumoto, S. Sakaguchi, T. Ohsita, and A. Oгуra, *J-PV*, 4, 581 (2014).
5. B. Hox, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.*, 89, 042112 (2006).
6. A. G. Abele, T. Lauinger, J. Schmidt, and R. Hezel, *Appl. Phys. Lett.*, 66, 2828 (1995).
7. H. Lee, T. Tachibana, N. Ikeno, H. Hashiguchi, K. Arafune, H. Yoshida, S. Satoh, T. Chikyow, and A. Oгуra, *Appl. Phys. Lett.*, 100, 143901 (2012).
8. S. Miyajima, I. Irikawa, A. Yamada, and M. Konagai, *Appl. Phys. Express*, 3, 012301 (2010).
9. M. Schaper, J. Schmidt, H. Plagwiz, and R. Brednel, *Prog. Photovolt: Res. Appl.*, 13, 381 (2005).
10. D. Zellke, J. H. Petermann, F. Werner, B. Veith, R. Brednel, and J. Schmit, *J. Phys. State Solid: Rapid Res. Lett.*, 5, 298 (2011).
11. A. G. Abele, S. Glunz, and W. Warta, *Sol. Energy Mater. Sol. Cells*, 29, 175 (1993).
12. S. W. Glunz, D. Biro, S. Rein, and W. Warta, *J. Appl. Phys.*, 86, 683 (1999).
13. B. Hox, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.*, 89, 042112 (2006).
14. B. Liu, A. Popot, Z. Deng, H. P. Benner, A. Rohatgi, P. Sanu, S. K. Estreicher, Y. K. Park, and M. A. Roberson, *Sol. Energy Mater. Sol. Cells*, 41/42, 159 (1996).
15. K. Arafune, S. Miki, R. Matsuani, J. Hamano, H. Yoshida, T. Tachibana, H. Lee, A. Oguira, T. Ohsita, and S. Satoh, *Jpn. J. Appl. Phys.*, 51, 014SD06 (2012).
16. K. Arai, *Tech. Digest First International Photovoltaic Science and Engineering Conference*, Kobe, 1984, p37.
17. A. G. Abele, *Sol. Energy Mater. Sol. Cells*, 65, 239 (2001).
18. A. G. Abele and R. Hezel, *Prog. Photovolt: Res. Appl.*, 5, 29 (1997).
19. K. H. Hwang, E. Yoon, K. Whang, and J. Y. Lee, *J. Appl. Phys. Lett.*, 67, 3590 (1995).
20. K. H. Hwang, J. W. Park, E. Yoon, K. W. Whang, and J. Y. Lee, *J. Appl. Phys.*, 81, 74 (1997).
21. J. Schmidt and A. G. Abele, *J. Appl. Phys.*, 85, 3626 (1999).
22. J. Schmidt, F. M. Schuermann, W. C. Sinke, S. W. Glunz, and A. G. Abele, *Appl. Phys. Lett.*, 71, 252 (1997).
23. S. Steingrube, P. P. Altermatt, T. Schurmann, J. Schmidt, and R. Brednel, *J. Appl. Phys. Lett.*, 108, 014506 (2010).
24. F. J. Na, G. G. Samudra, M. Peters, A. G. Abele, F. Werner, J. Schmidt, and B. Hox, *J. Appl. Phys.*, 112, 054508 (2012).
25. S. Reim, *Lifetime spectroscopy: A method of defect characterization in silicon for photovoltaic applications*, Springer 2004, Berlin, Germany.
26. K. Higashine, H. Koyama, H. Oda, T. Kurosawa, H. Matsumura, and N. Otsuka, *J. Vac. Sci. Technol. B*, 30, 032108 (2012).
27. N. Stoddard, A. Karoui, G. Duscher, A. Kvit, and G. Rozgonyi, *Electrochem. Solid-State Lett.*, 6, G134 (2003).
28. G. S. Oehrlein, R. M. Tromp, Y. H. Lee, and E. J. Petroll, *Appl. Phys. Lett.*, 45, 420 (1984).
29. G. S. Oehrlein, *Mater. Sci. Eng. B*, 4, 441 (1989).
30. T. Tachibana, D. Takai, Y. Yamashita, N. Ikeno, H. Tokutake, K. Nagata, A. Oguira, and Y. Ohsita, *29th European Photovoltaic Solar Energy Conference and Exhibition*, 2014.