Experimental evidence of staggered oxygen dimers as a component of boron-oxygen complexes in silicon

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We have investigated the relationship of the boron-oxygen (B-O) complexes to the staggered oxygen dimers (O_{2i}^{st}) in silicon. It is found that the saturated concentration of B-O complexes (N_t^*) is proportional to the O_{2i}^{st} concentration ($[O_{2i}^{st}]$) in Czochralski silicon samples, whose $[O_{2i}^{st}]$ are varied by annealing at different temperatures. This proportionality is further confirmed in a special silicon ingot with variable oxygen and carbon concentrations, in which the N_t^* and $[O_{2i}^{st}]$ show the similar dependences on the interstitial oxygen concentration. Therefore, our experimental data support that the O_{2i}^{st} should be an ingredient of the light-induced defects in silicon. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4793660]

The light-induced degradation phenomenon (LID) limits the improvement of conversion efficiencies of boron-doped silicon solar cells, which is due to the generation of boron-oxygen (B-O) recombination centers under light illumination.[1] The saturated concentration of B-O complexes (N_t^*) has been found to be proportional to boron concentration (N_B)[2] (actually the hole concentration p_0)[3] and the square of interstitial oxygen concentration ($[O_i]^2$).[4] Hence, Schmidt *et al.* proposed the B_sO_{2i} model, which is composed of a substitutional boron atom (B_s) and an interstitial oxygen dimer (O_{2i}).[4] And many explanations for the behavior of LID[5–7] and other models[8,9] were also based on the assumption that O_{2i} is directly involved in the generation of light-induced recombination centers in silicon. The reasons are that the O_{2i} has the same quadratic dependence on the interstitial oxygen atoms,[10] and meanwhile it is regarded as a fast diffusing species to explain the observed LID process. First-principles calculations have revealed that the ground state of O_{2i} is the staggered dimer (O_{2i}^{st}) in which two O_i atoms lie at the neighboring bond center sites in a {110} plane.[11–14] It is believed that the O_{2i} can diffuse by the restructuring between the O_{2i}^{st} and the squared dimer (O_{2i}^{sq}) configuration in ⟨110⟩ chains with diffusion barrier of 1.0–1.5 eV at their neutral states,[14–17] and the barrier will be further reduced to about 0.3 eV through Bourgoin-Corbett mechanism.[6,18] Moreover, the O_{2i}^{sq} is calculated to have deep donor levels in the energy gap and then maybe the origin of the effective recombination activity of B-O complexes.[9,17]

However, there is still lack of direct evidence on the correlation of the O_{2i} with the B-O complexes. The independent quadratic dependence of N_t^* and $[O_{2i}]$ on the $[O_i]$ cannot firmly prove that the O_{2i}, especially the O_{2i}^{st}, is a component of B-O complex. Murin *et al.*[19] reported that they found no clue of the existence of the doubly positively charged oxygen dimer (O_{2i}^{++}) and doubted whether the O_{2i} can play the central role in the formation of B-O complexes. Hence, the relationship between the O_{2i} and B-O complex in silicon is still an open question. In this paper, we find the proportionality between the N_t^* and $[O_{2i}^{st}]$ in boron-doped Czochralski (Cz) silicon. Moreover, this proportionality is further convinced in a special silicon ingot with an approximately fixed N_B, but variable oxygen $[O_i]$ and carbon concentration ($[C_s]$). Our results support the assumption that the O_{2i} can be directly involved in the generation of B-O complexes in silicon.

The samples used in this work were cut from a Cz silicon ingot and a mono-like silicon ingot both with boron-doping, in which the resistivity was 2.0 and 1.7 Ω cm, respectively. The $[O_i]$ and $[C_s]$ were determined by a Fourier transformed infrared spectroscope (FTIR, Bruker IFS 66v/s). The $[O_i]$ was found to be 9×10^{17} cm^{-3} in the Cz silicon samples and the $[C_s]$ was below the detection limit. The mono-like silicon sample of $120 \times 20 \times 2$ mm^3 showed steep axial gradients of $[O_i]$ and $[C_s]$, with the $[O_i]$ in the range of $3–8 \times 10^{17}$ cm^{-3} and the $[C_s]$ $0.5–5 \times 10^{17}$ cm^{-3}. The Cz silicon samples were first deposited with silicon-nitride (SiN$_x$:H) layers on both surfaces to protect from the metallic contamination, and then they were subjected to isothermal annealing in the temperature range of 650–900 °C for 0.5 h, respectively. The samples annealed at 550 °C and 600 °C were kept for longer time to ensure that their equilibrium concentrations of O_{2i} are obtained. Afterwards, these samples were quenched to room temperature and dipped into HF solution to remove the SiN$_x$ layer. Again, the SiN$_x$:H layers were deposited with PECVD to get good surface passivation. Note that a Ga-doped silicon deposited with the SiNx:H film under the same condition has been used as the reference to inspect the stability of passivation layer. The mono-like sample was subjected to the phosphorus-diffusion gettering at 900 °C for 1 h to getter metallic impurities. After etching the diffused layers, it was also coated with SiN$_x$:H layers.

In order to fully generate the B-O complexes, the samples were illuminated under halogen lamp with an intensity of 30 mW/cm^2 for 48 h, and then kept in dark for 16 h to ensure that the residual iron in samples was in the form

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of iron-boron pair. The degraded carrier lifetime (τ_d) was measured using the quasi-steady-state photoconductance (QSSPC) technique. And the B-O complexes were annihilated by annealing at 250 °C for 10 min. Before measuring the carrier lifetime after annihilation (τ_0), the samples were also kept in dark for 16 h. The evolution of $[O_{2i}^{st}]$ in all these samples was monitored by measuring the IR absorption spectra at 10 K with a spectral resolution of 1 cm^{-1}.

Figure 1 shows the IR absorption spectra of Cz silicon samples annealed at 650 and 900 °C for 0.5 h. The absorption band at 1085 cm^{-1} is the local vibration mode (LVM) related to the oxygen isotopes ^{18}O. The absorption bands at 1012, 1060, and 1105 cm^{-1} are associated to the O_{2i}.[10] Among them, the 1105 cm^{-1} band has been assigned to the skewed dimer (O_{2i}^{sk})[13] in which the two O_i atoms are located in the crossed {110} planes and are separated by two silicon atoms.[13,20] The 1012 and 1060 cm^{-1} bands are related to the O_{2i}^{st} and they are originated from the splitting of 1136 cm^{-1}, the LVM of O_i at low temperature,[21,22] due to the interaction within the two neighboring O_i atoms. In order to measure the $[O_{2i}^{st}]$, here, we adopt the calibration coefficient (f) for the 1012 cm^{-1} to be half of f_{1136}, which is obtained to be 2.36×10^{16} cm^{-2} at 10 K. Note that this f_{1136} corresponds to the integrated intensity of 1136 cm^{-1}. For simplicity, the same f is also adopted for 1105 cm^{-1} to the $[O_{2i}^{sk}]$.

Fig. 2 shows the $[O_{2i}^{st}]$, $[O_{2i}^{sk}]$ in the Cz silicon samples by measuring the intensity of 1012 and 1105 cm^{-1} in the FTIR spectra, respectively. When the samples are annealed at high temperature, the O_{2i} will associate or dissociate to reach their equilibrium concentrations $[O_{2i}]^{eq}$. According to the mass action law, the $[O_{2i}]^{eq}$ can be expressed as[10]

$$\frac{[O_{2i}]^{eq}}{[O_i]^2} = \frac{c}{\rho} \exp\left(\frac{E_b}{kT}\right), \qquad (1)$$

where E_b is the binding energy of O_{2i}, ρ is the lattice site density and c is a constant. From the figure, the E_b are obtained to be 0.13 and 0.03 eV for O_{2i}^{st} and O_{2i}^{sk}, respectively, which are less than the previous reported binding energies, 0.3 and 0.2 eV. Here, the measured $[O_{2i}]$ may be somewhat different from the $[O_{2i}]^{eq}$ if the cooling rate is insufficient to reserve all the O_{2i} in its equilibrium state.
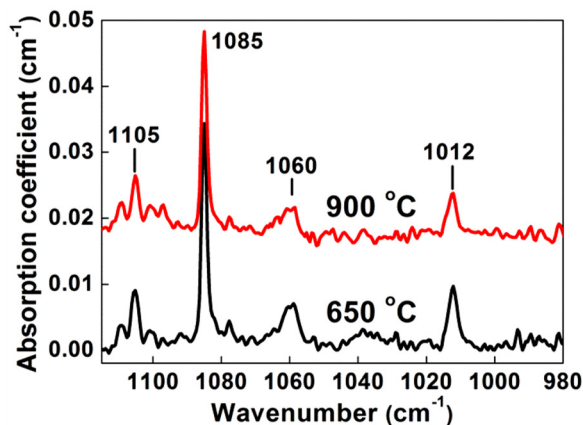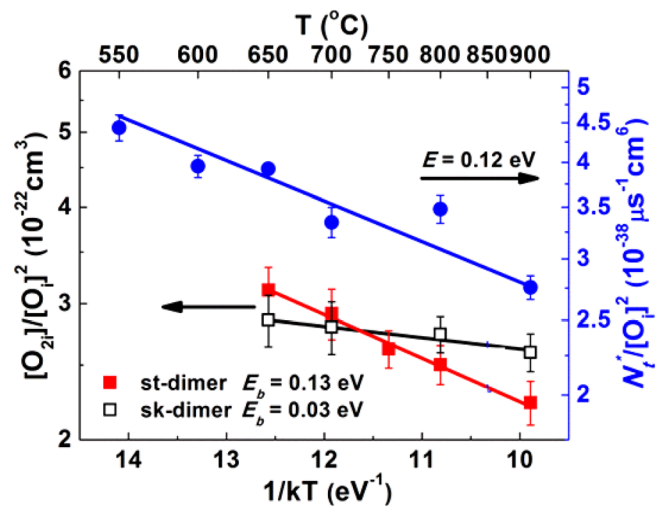

FIG. 2. Arrhenius plots of the $[O_{2i}^{st}]$, $[O_{2i}^{sk}]$ and the saturated concentration of B-O complexes N_t^* in the Cz-Si samples annealed at different temperatures, normalized to the square of interstitial oxygen concentration.

Fig. 2 also plots the N_t^* in the Cz silicon samples with treatment of annealing at different temperatures. It is well known that the effective defect concentration N_t is calculated with the following expression:

$$N_t \equiv \frac{1}{\tau(t)} - \frac{1}{\tau_0} = \frac{1}{\tau_{BO}}, \qquad (2)$$

where τ_{BO} is the lifetime limited by the B-O complexes. The measured carrier lifetime $\tau(t)$ is obtained at a fixed excess-carrier injection level of $0.05N_B$. We examine that the degradation of effective lifetime under the illumination for 48 h has already become stable and then the saturated concentration N_t^* is calculated with the τ_d (t = 48 h) and τ_0. Note that the effective lifetime in referenced sample, gallium-doped Cz silicon, keeps almost the same during the whole illumination process, indicating that the SiN$_x$:H layer is quite stable. As can be seen from the figure, the concentrations of B-O complexes will be reduced in silicon after annealing at high temperatures. Derived from the Arrhenius plots in the figure, the slope gives an activation energy E of 0.12 eV, though it shows a large uncertainty due to the data scattering. Previously, Rougieux *et al.*[23] reported a quite similar result that E is 0.14 eV. Interestingly, it can be found that that the E_b for O_{2i}^{st} is very close to the activation energy for the N_t^* in our Cz silicon samples, but the E_b for O_{2i}^{sk} diverges significantly. Hence, we believe that the N_t^* is proportional to the $[O_{2i}^{st}]$ but not to $[O_{2i}^{sk}]$. Coutinho *et al.*[14] have calculated that the transition between O_{2i}^{sk} and O_{2i}^{st} has to surmount a barrier of 2.2 eV, meaning that the O_{2i}^{sk} can hardly diffuse at a large rate and is not possible to participate in the generation of B-O complexes.

Figure 3 shows the IR spectra from two different positions (A and B) of mono-like silicon sample with different oxygen and carbon concentrations. In position A, the $[O_i]$ and $[C_s]$ are 7.7×10^{17} and 5×10^{16} cm^{-3}, respectively, while 2.7×10^{17} and 4.1×10^{17} cm^{-3} in position B. In the spectrum of position A, besides the bands of 1012, 1060, and 1105 cm^{-1} for O_{2i}, some other bands at 1052, 1078, 1099, 1104 cm^{-1} are observed as well, which might be attributed

FIG. 1. Infrared absorption spectra measured at 10 K with the resolution of 1 cm^{-1} for the Cz-Si samples annealed at 650 and 900 °C for 0.5 h, respectively. The spectra are shifted on the vertical axis for clarity.
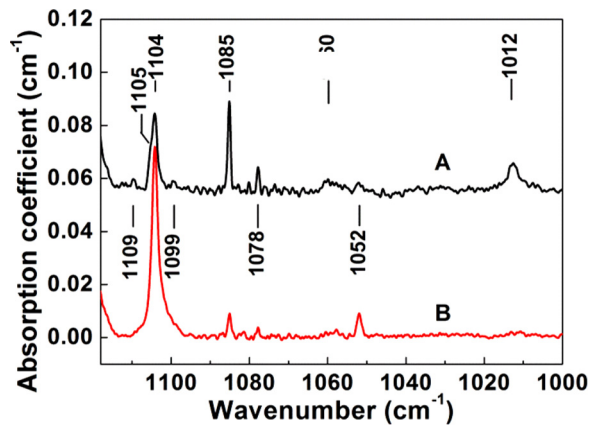
FIG. 3. Infrared absorption spectra measured at 10 K with the resolution of 1 cm^{-1} for two positions at the mono-like silicon sample (A: carbon-lean and B: carbon-rich). The spectra are shifted on the vertical axis for clarity.

to carbon-oxygen (C-O) complexes. Newman *et al.*[24–26] have claimed that 1104 cm^{-1} band is attributed to C_sO_i complex. And the bands of 1052 and 1099 cm^{-1} have been reported to associate with C_sO_{2i} complex,[27–29] so those two bands may be originated from the shift of 1012 and 1060 cm^{-1} for O_{2i} by the C_s atoms. Spectrum A shows that the intensity of 1052 cm^{-1} is about 1/4 of the 1012 cm^{-1}, meaning that nearly a quarter of the O_{2i}^{st} are captured by the C_s atoms and form the C_sO_{2i} complexes. With a much higher $[C_s]$ in position B, the 1012 cm^{-1} becomes negligible but the 1052 cm^{-1} still increases, indicating that most of the O_{2i} may be reserved in the form of C_sO_{2i} complexes. Therefore, the variable $[C_s]$ will change the dependence of $[O_{2i}^{st}]$ on the $[O_i]$ along the ingot. Thus, if the N_t^* has a correlation with $[O_{2i}^{st}]$, it will still increase with the $[O_i]$ in the same way as the $[O_{2i}^{st}]$. Figure 4 shows the dependence of N_t^* and $[O_{2i}^{st}]$ on the $[O_i]$ in the mono-like silicon sample and the inset shows the distribution of $[O_i]$ and $[C_s]$. It can obviously be seen that both the N_t^* and $[O_{2i}^{st}]$ show the similar dependence on the $[O_i]$. This further proves the proportionality between the N_t^* and the $[O_{2i}^{st}]$ and supports the assumption that the staggered O_{2i} is the crucial ingredient for the generation of B-O recombination centers in silicon.

Comparing the present models of B-O complexes, the B_sO_{2i} and B_iO_{2i} model,[4–8] the O_{2i} plays different roles in
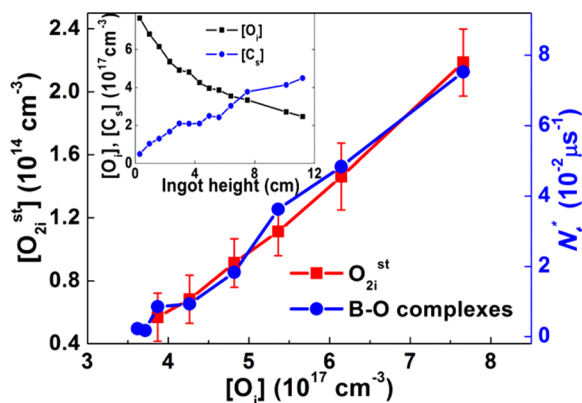

FIG. 4. Plots of the staggered oxygen dimer concentration $[O_{2i}^{st}]$ and the saturated concentration of B-O complexes N_t^* as a function of $[O_i]$. The inset is the distributions of interstitial oxygen concentration $[O_i]$ and substitutional carbon concentration $[C_s]$ in the mono-like silicon sample.

them. In the standard B_sO_{2i} model, the mobile O_{2i} diffuses randomly until it is captured by the B_s atom to form the B_sO_{2i} complex. While in B_iO_{2i} model, the O_{2i} acts as a trap and absorbs the mobile B_i atom. The trapped B_iO_{2i} is the latent center for the recombination center through reconfiguration. Though these two models can be used to explain the proportionality between the N_t^* and the $[O_{2i}^{st}]$, they are not fully consistent with the observed results, e. g., $N_t^* \sim p_0$ and the generation rate constant $R_{gen} \sim p_0^2$.[3,30] We think that a "hybrid" model seems possible to be a candidate for the explanation of LID, in which the O_{2i}^{st} is trapped by B_s atom within a small distance, separated by one or several silicon atoms, and this trapped species acts as the latent center (LC).[31] Since the $[O_{2i}^{st}]$ is much smaller than the N_B, the concentration of the grown-in LC will be limited by $[O_{2i}^{st}]$. Therefore, the final N_t^* will be proportional to $[O_{2i}^{st}]$. It is reasonable to consider that the O_{2i}^{st} has a very deep donor (0/+) close to the valence band, so a portion of O_{2i}^{st} will be single charged, depending on the Fermi level. When the band-gap illumination or forward-bias is applied, the O_{2i}^{st+} will capture an electron and become the excited O_{2i}^{st0} by utilizing the energy released during the electron-capture process. Then the metastable O_{2i}^{st0} captures a pair of holes quickly and transforms to the doubly charged O_{2i}^{sq++}. Afterwards, the O_{2i}^{sq++} will capture a pair of electron and transform to the O_{2i}^{st0} again. Finally, the O_{2i}^{st0} in the LC state will diffuse to the nearest site of B_s atom forming the recombination centers $B_s^-O_{2i}^{sq++}$. Among the diffusive steps, the transformation from O_{2i}^{st0} to O_{2i}^{sq++} through the recombination-enhanced mechanism[32] is the rate-limited step, hence it can be concluded that the R_{gen} will be proportional to p_0^2, and meanwhile the N_t^* will be limited by the concentration of O_{2i}^{st+} and then proportional to p_0. According to this model, the process of LID should be a process of hole-trapping which has been well confirmed by Crandall using the junction-capacitance methods.[33] His experiment also demonstrated that the capacitance change incurred by the generation of B-O recombination centers is very small, indicating that only a very small portion of O_{2i}^{st} have transformed into the O_{2i}^{sq++} which is in consistent with our model. Murin *et al.*[19] reported that they cannot find the existence of the O_{2i}^{sq++} using FTIR. Similarly, we have measured the IR absorption spectra at 10 K before and after the illumination for 48 h, however no noticeable difference was observed. Hence, the reason for the failure to find the O_{2i}^{sq++} by FTIR should be due to the too low $[O_{2i}^{sq++}]$ to be detected by FTIR.

In summary, we have studied the correlation of B-O complexes with the O_{2i} in silicon. It is found that the N_t^* and $[O_{2i}^{st}]$ in Cz silicon have the similar dependence on the annealing temperature, with quite close binding energies, meaning that the N_t^* is proportional to the $[O_{2i}^{st}]$. In the mono-like silicon, though the $[O_{2i}^{st}]/[O_i]^2$ is influenced by the formation of C_sO_{2i} complexes, the proportionality between the N_t^* and $[O_{2i}^{st}]$ is still established. These findings suggest that the O_{2i}^{st} is one ingredient of B-O complexes. Hence, the method of reducing the $[O_{2i}^{st}]$ should be effective to suppress the generation of B-O complexes. It is well proved in isovalent impurity atoms (C, Ge and Sn) doped Cz silicon,[34–36] which have the lower $[O_{2i}^{st}]$ and then the lower LID effect, compared to the conventional Cz silicon.

[1] J. Schmidt, A. G. Aberle, and R. Hezel, in *Proceedings of the 26th IEEE Photovoltaic Specialists Conference, Anaheim, CA* (IEEE, New York, 1997), p. 13.

[2] T. Saitoh, H. Hashigami, S. Rein, and S. Glunz, Prog. Photovoltaics **8**, 537 (2000).

[3] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. D. Sabatino, and L. J. Geerligs, J. Appl. Phys. **105**, 093704 (2009).

[4] J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004).

[5] D. W. Palmer, K. Bothe, and J. Schmidt, Phys. Rev. B **76**, 035210 (2007).

[6] J. Adey, R. Jones, D. W. Palmer, P. R. Briddon, and S. Öberg, Phys. Rev. Lett. **93**, 055504 (2004).

[7] M. H. Du, H. M. Branz, R. S. Crandall, and S. B. Zhang, Phys. Rev. Lett. **97**, 256602 (2006).

[8] V. V. Voronkov and R. Falster, J. Appl. Phys. **107**, 053509 (2010).

[9] V. V. Voronkov, R. Falster, K. Bothe, B. Lim, and J. Schmidt, J. Appl. Phys. **110**, 063515 (2011).

[10] L. I. Murin, T. Hallberg, V. P. Markevich, and J. L. Lindström, Phys. Rev. Lett. **80**, 93 (1998).

[11] M. Needels, J. D. Joannopoulos, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **43**, 4208 (1991).

[12] P. Deák, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **45**, 11612 (1992).

[13] M. Pesola, J. von Boehm, and R. M. Nieminen, Phys. Rev. Lett. **82**, 4022 (1999).

[14] J. Coutinho, R. Jones, P. R. Briddon, and S. Öberg, Phys. Rev. B **62**, 10824 (2000).

[15] D. Åberg, B. G. Svensson, T. Hallberg, and J. L. Lindström, Phys. Rev. B **58**, 12944 (1998).

[16] M. Ramamoorthy and S. T. Pantelides, Solid State Commun. **106**, 243 (1998).

[17] Y. J. Lee, J. von Boehm, M. Pesola, and R. M. Nieminen, Phys. Rev. B **65**, 085205 (2002).

[18] J. C. Bourgoin and J. W. Corbett, Phys. Lett. A **38**, 135 (1972).

[19] L. I. Murin, E. A. Tolkacheva, V. P. Markevich, A. R. Peaker, B. Hamilton, E. Monakhov, B. G. Svensson, J. L. Lindström, P. Santos, J. Coutinho, and A. Carvalho, Appl. Phys. Lett. **98**, 182101 (2011).

[20] S. Öberg, C. P. Ewels, R. Jones, T. Hallberg, J. L. Lindström, L. I. Murin, and P. R. Briddon, Phys. Rev. Lett. **81**, 2930 (1998).

[21] D. R. Bosomworth, W. Hayes, A. R. L. Spray, and G. D. Watkins, Proc. R. Soc. London **A317**, 133 (1970).

[22] O. D. Gryse and P. Clauws, J. Appl. Phys. **87**, 3294 (2000).

[23] F. E. Rougieux, B. Lim, J. Schmidt, M. Forster, D. Macdonald, and A. Cuevas, J. Appl. Phys. **110**, 063708 (2011).

[24] R. C. Newman and R. S. Smith, J. Phys. Chem. Solids **30**, 1493 (1969).

[25] A. R. Bean and R. C. Newman, J. Phys. Chem. Solids **33**, 255 (1972).

[26] H. Yamanaka, Jpn. J. Appl. Phys., Part 1 **33**, 3319 (1994).

[27] Y. Shirakawa and H. YamadaKaneta, J. Appl. Phys. **80**, 4199 (1996).

[28] L. I. Murin, V. P. Markevich, J. L. Lindström, M. Kleverman, J. Hermansson, T. Hallberg, and B. G. Svensson, Solid State Phenom. **82**, 57 (2002).

[29] C. A. Londos, E. N. Sgourou, A. Chroneos, and V. V. Emtsev, Semicond. Sci. Technol. **26**, 105024 (2011).

[30] M. Forster, E. Fourmond, F. E. Rougieux, A. Cuevas, R. Gotoh, K. Fujiwara, S. Uda, and M. Lemiti, Appl. Phys. Lett. **100**, 042110 (2012).

[31] P. Chen, X. Yu, Y. Wu, J. Zhao, and D. Yang, J. Appl. Phys. **112**, 084509 (2012).

[32] R. S. Crandall, J. Appl. Phys. **108**, 103713 (2010).

[33] J. D. Weeks, J. C. Tully, and L. C. Kimerling, Phys. Rev. B **12**, 3286 (1975).

[34] X. Yu, P. Wang, P. Chen, X. Li, and D. Yang, Appl. Phys. Lett. **97**, 051903 (2010).

[35] X. Yu, P. Wang, and D. Yang, Appl. Phys. Lett. **97**, 162107 (2010).

[36] M. K. Kang, J. Hong, I. Cooper, A. Ebong, B. Rounsaville, and A. Rohatgi, J. Electrochem. Soc. **158**, H724 (2011).