Size-dependent photocurrent of photodetectors with silicon nanocrystals

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We report on the effect of nanocrystal size on the photocurrent of silicon nanocrystal (Si NC) photodetectors. The photocurrent onset energy was increased with decreasing the size of Si NCs, which agreed with the blueshift in the absorption onset. The increase in the quantum efficiency with increasing the size of Si NCs was much larger than the increase in the absorbance with increasing the size of Si NCs. This was attributed to the differences in charge separation for Si NC of different sizes, which was influenced by the recombination rate and binding energy of photogenerated excitons in Si NCs. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3130086]

Silicon nanocrystals (Si NCs) have been shown to possess intriguing properties, such as bandgap control with NC size,[1–3] very fast optical transition,[4] and multiple carrier generation.[5] These properties have made Si NCs useful in various devices, such as light-emitting devices,[6–8] solar cells,[9–11] and photodetectors.[12–16] Recently, the size-dependent properties of Si NCs were studied to realize silicon-based wavelength-sensitive photodetectors without using color filters,[12] because it has been shown that the absorption onset energy of silicon can be controlled by using quantum confinement effects in Si NCs.[2] Although a few reports have demonstrated photodetectors using Si NCs embedded in silicon oxide[13,14] and silicon nitride,[15] there has been no report on the relationship between the size of Si NCs and the photocurrent of Si NC photodetectors. Moreover, a clear relationship between the absorption in Si NCs and the photocurrent of Si NC photodetectors has never been reported because most studies[12,14–16] have been performed with diode or transistor structures, where the photocurrent is heavily affected by the current from silicon wafers. Furthermore, there is some disagreement over the origin of photoresponse, as a recent study[16] has shown, that the photocurrent of photodetectors with Si NCs embedded in silicon oxide is generated by the absorption of light in the interface states between Si NCs and silicon oxide.

In this report, we investigated the effect of Si NC size on the photoresponse of Si NC photodetectors. This size-dependent photoresponse agreed well with the shift in absorption onsets of Si NCs. We also show that the photocurrent of photodetectors is related to the absorbance of Si NCs and to the separation of photogenerated excitons, which is affected by the size of Si NCs. Finally, we show that the photocurrent of photodetectors with Si NCs embedded in silicon nitride is originated from the absorption of light in Si NCs, not from the interface states.

Silicon nitride films, in which Si NCs were spontaneously formed during the film growth, were deposited on *n*-type silicon (100) wafers with a low resistivity of 0.002 Ω cm at 300 °C by plasma-enhanced chemical vapor deposition using SiH_4 and NH_3 as the source gases. The size of Si NCs in the silicon nitride films was controlled by changing the gas ratio of SiH_4 and NH_3.[17] The size of Si NCs was determined from the relationship between the photoluminescence (PL) peak position and Si NC size.[17] Detailed deposition conditions for the silicon nitride films with Si NCs are shown in Table I. The absorption onsets were determined from the extinction coefficients measured using an ellipsometer. For current-voltage (*I-V*) measurements, 300 $\times$ 300 μm^2 photodetectors were defined on the wafers by photolithography. A 200 nm thick In_2O_3:Sn film [indium tin oxide (ITO)] was deposited over the silicon nitride films with Si NCs, and 100 nm thick aluminum layers as front grid and back metal electrodes were deposited over ITO and behind Si wafers by e-beam evaporation. Light-emitting diodes (LEDs) with emission energies of 3.1 eV (400 nm, UV), 2.64 eV (470 nm, blue), 2.34 eV (530 nm, green), 2.14 eV (580 nm, yellow), and 1.77 eV (700 nm, red) were used as light sources for photocurrent measurements.

Figure 1(a) shows a cross-sectional transmission electron microscopy (TEM) image of silicon nitride films with 4.0 nm Si NCs. Crystalline silicon phase is confirmed from the lattice image, as shown in the inset of Fig. 1(a), and the Si NC density is estimated as $1.5\times10^{12}/cm^2$. Figure 1(b) shows the size-dependent absorption onsets of Si NCs, which were determined from extinction coefficients. It has been reported that the bandgap energy of three-dimensionally confined Si NCs can be fitted as $E(\text{eV})=E_{\text{bulk}}+C/d^2$ based on the effective mass theory, where E_{bulk} is the bandgap energy of bulk silicon, C is a quantum confinement parameter, and d is the diameter of Si NCs.[2] As shown in Fig. 1(b), the absorption onsets of Si NCs are fitted as $E(\text{eV})=1.13+20.1/d^2$, indicating that the change in the absorption onsets of Si NCs is due to quantum confinement effect.

TABLE I. The deposition condition and the size of Si NCs determined from the PL peak using the equation in Ref. 17.

5% SiH_4 in N_2 (SCCM)	NH_3 (SCCM)	Si NC size (nm)
100	30	3.3
100	15	3.6
100	5	4.0
200	5	4.7

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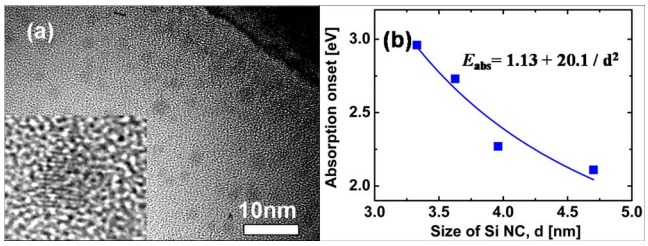

FIG. 1. (Color online) (a) A cross-sectional TEM image of Si NCs. The darker image in the upper-right part of this figure is the silicon wafer substrate. (b) Measured absorption onsets (square) and fitted curve (solid line) plotted against the size of Si NCs.

Figure 2 shows the *I-V* curves of Si NC photodetectors under LED illumination. Because the *n*-type silicon wafer has a very low resistivity of 0.002 Ω cm, there is negligible depletion region in the silicon wafer. Therefore, a very small amount of current from the silicon wafer is expected to contribute to the measured photocurrent. Figure 2(a) shows that the photodetectors with 3.3 nm Si NCs do not show any increase in photocurrent under all LED illumination although the absorption onset energy of 2.96 eV of 3.3 nm Si NCs, as shown in Fig. 1(b), is smaller than 3.1 eV energy of UV LED light. This result will be explained later. The photocurrent of photodetectors with 3.6 nm Si NCs is increased only under UV light, because the energy of the UV light is greater than the absorption onset energy of 2.73 eV of 3.6 nm Si NCs, as shown in Fig. 1(b). The absorption onset energy of 4.0 nm Si NCs is 2.27 eV and a positive photoresponse is observed under UV, blue (2.64 eV), and green (2.34 eV) light, as shown in Fig. 2(c). The absorption onset energy of 4.7 nm Si NCs is 2.11 eV, and a positive photoresponse is shown under all UV, blue, green, and yellow (2.14 eV) lights, as shown in Fig. 2(d). Figure 2 clearly shows that the photoresponse of Si NC photodetectors is strongly related to the absorption onset of Si NCs. Figure 2 also shows that the photocurrent of Si NCs increases with increasing the energy of photons and with increasing the size of Si NCs. This result is attributed to the increase in the density of state (DOS). The absorbance is related to the DOS of Si NCs which is proportional to $(E_{\text{photon}}-E_g)^2$, where E_{photon} is the exciting photon energy and E_g is bandgap energy.[18] For this reason, the photocurrent of Si NCs increases as the exciting photon energy E_{photon}

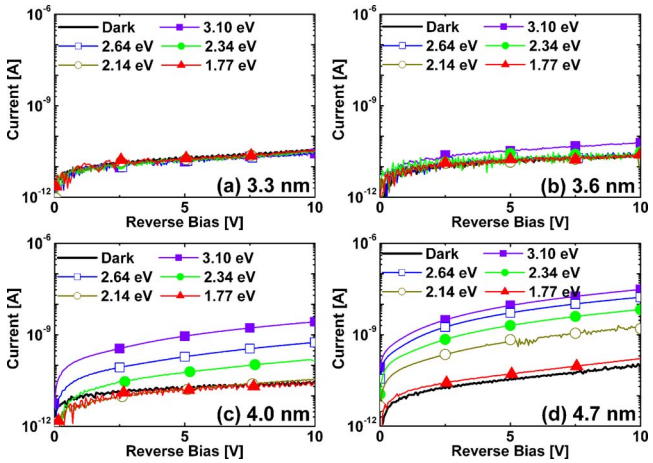

FIG. 2. (Color online) *I-V* curves of photodetectors with the size of Si NCs (film thickness is 300 nm). (a) 3.3 nm Si NCs, (b) 3.6 nm Si NCs, (c) 4.0 nm Si NCs, and (d) 4.7 nm Si NCs.

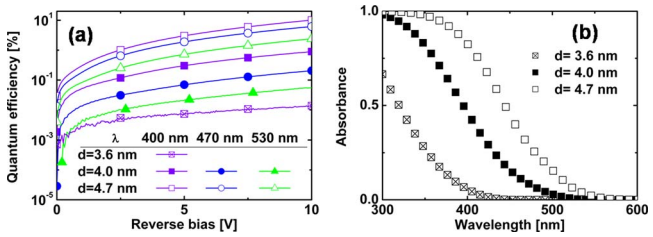

FIG. 3. (Color online) (a) Quantum efficiency calculated from *I-V* curves of Figs. 2(b)–2(d). (b) Absorbance of 3.6, 4.0, and 4.7 nm Si NCs.

increases. The DOS of Si NCs also increases as the bandgap shrinks with increasing the size of NCs, as shown in Fig. 1(b), resulting in the increased absorbance and photocurrent for larger Si NCs.

Figure 3(a) shows that the quantum efficiency of photodetectors with 3.6, 4.0, and 4.7 nm Si NCs. Quantum efficiency is calculated from the measured photocurrent and LED output power, using the following equation: Quantum efficiency=(photocurrent/e)/(optical power/$h\nu$), where e is electronic charge and $h\nu$ is photon energy.[19] Figure 3(a) shows that the quantum efficiency of photodetectors with 4.7 nm Si NCs at 10 V is 11.3, 30.1, and 43.6 times larger than that of photodetectors with 4.0 nm Si NCs at 10 V under the exciting light with wavelengths of 400 nm (3.1 eV), 470 nm (2.64 eV), and 530 nm (2.34 eV), respectively. However, the absorbance of Si NCs increases only by 1.8, 3.4, and 14.1 times at 400, 470, and 530 nm, respectively, as the size of Si NCs increases from 4.0 to 4.7 nm, as shown in Fig. 3(b). This result clearly indicates that the quantum efficiency decreases more sharply in comparison with the absorbance as the size of Si NC decreases. This feature is more evident in the case of 3.6 and 4.0 nm Si NCs, where the difference in quantum efficiency at a wavelength of 400 nm is 7.8 times larger than the difference in absorbance, as shown in Fig. 3. The much larger size-dependent quantum efficiency than the absorbance of Si NCs is attributed to the faster exciton recombination rate and larger exciton binding energy of smaller Si NCs. The exciton binding energy (E_b) of Si NCs can be estimated by using the equation, $E_b=(1.8q^2)/(2\pi\varepsilon_0\varepsilon_{\text{NC}}d)$, where q is the electronic charge, d is the diameter of Si NCs, ε_0 and ε_{NC} are the dielectric constants of free space and Si NCs, respectively.[20] The E_b of Si NCs are 133, 122, 110, and 93 meV for 3.3, 3.6, 4.0, and 4.7 nm Si NCs, respectively, when ε_{NC} is assumed to be the same as that of bulk Si. Exciton dissociation efficiency can be related to E_b as $\exp(-E_b/kT)$, where k is the Boltzmann's constant and T is the ambient temperature.[21] And this predicts that the exciton dissociation efficiency for 4.0 nm Si NCs is 1.6 times larger than that of 3.6 nm Si NCs. The larger E_b of smaller NCs will hinder the separation of photogenerated excitons,[22] and the faster exciton recombination rate of smaller NCs also will reduce the generation of electron-hole pairs.[4] The fact that no photoresponse was observed for 3.3 nm Si NCs under UV LED, as shown in Fig. 2(a), can also be attributed to the faster recombination rate and larger E_b of smaller Si NCs.

Figures 1–3 show that the size-dependent photocurrent of Si NCs can be attributed to the shift in absorption onset due to quantum confinement effect. Meanwhile, it has been reported that the absorption of light in the interface state is the origin of the photoresponse in the photodetectors with Si

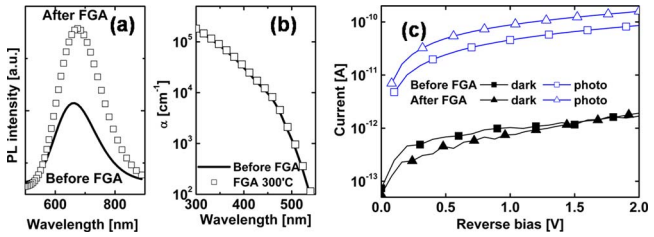

FIG. 4. (Color online) Effect of FGA on properties of 4.0 nm Si NCs and photodetectors with 4.0 nm Si NCs. (Film thickness is 100 nm and the light source is a blue LED with an emission energy of 2.64 eV). (a) PL intensity, (b) absorption coefficients (α), and (c) dark and photo *I-V* curves.

NCs embedded in silicon oxide.[16] However, in the case of Si NCs embedded in Si nitride, there has been no clear explanation on the origin of the photoresponse of photodetectors. Figure 4(a) shows that the PL intensity of Si NCs is increased by a factor of 1.6 after forming gas annealing (FGA) (25% H_2–N_2) at 300 °C. The typical interface state in silicon nitride is silicon dangling bonds,[23] which functions as a nonradiative recombination center. These Si dangling bonds can be passivated by annealing in hydrogen atmosphere, as confirmed by the enhanced PL intensity of Si NCs,[24–26] which is consistent with the enhanced PL, as shown in Fig. 4(a). The absorption coefficients of Si NCs, however, were not changed after FGA at 300 °C for 2 h, as shown in Fig. 4(b). The results shown in Figs. 4(a) and 4(b) indicate that absorption is not related to the interface states. Figure 4(c) shows the effect of FGA on the *I-V* characteristics of Si NC photodetectors. The similar dark current and the increased photocurrent of Si NC photodetectors after FGA can be attributed to the passivation of interface states, indicating that absorption does not occur in the interface states. This result confirms that the photocurrent of photodetectors with Si NCs embedded in silicon nitride is originated from the absorption of light in Si NCs, not from the absorption at the interface states.

In summary, the effect of nanocrystal size on the photoresponse of Si NCs was investigated. The photoresponse of Si NCs was related to the absorption onset shift of Si NCs, which was affected by the size of Si NCs. The increase in the quantum efficiency with increasing the size of Si NCs was much larger than the corresponding increase in the absorbance. This was attributed to the difference in charge separation which was dependent on the recombination rate and binding energy of photogenerated excitons in Si NCs. It was also found that the photocurrent of Si NC photodetectors is not due to light absorption at the interface states but due to absorption in Si NCs.

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