Characterization of electronic structure of silicon nanocrystals in silicon nitride by capacitance spectroscopy

Chang-Hee Cho, Baek-Hyun Kim, Sang-Kyun Kim, and Seong-Ju Parka
Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea

(Received 26 January 2010; accepted 27 April 2010; published online 2 June 2010)

The electronic structure of silicon nanocrystals embedded in a silicon nitride insulating film is identified by using a capacitance spectroscopy. The tunneling capacitor device, which is used in this study, consists of a tunneling silicon nitride, an array of silicon nanocrystals embedded in a silicon nitride film, and a blocking silicon nitride deposited on p-type (100) Si substrate. The absolute position of the lowest conduction and the highest valence levels of the silicon nanocrystal is revealed and the band-gap energy of silicon nanocrystals estimated by the capacitance spectroscopy agrees well with that measured by photoluminescence spectroscopy. © 2010 American Institute of Physics. [doi:10.1063/1.3431572]

Semiconductor nanocrystals offer great promise for developing optical and electronic nanodevices because quantum confinement in nanocrystals leads to a variety of interesting optical and electronic properties.1–3 In particular, silicon nanocrystals have been intensively investigated since silicon is the most important material for modern electronics industry. In order to properly design the silicon nanocrystal devices, however, it is essential to know the absolute position of electronic energy levels of silicon nanocrystals. Optical spectroscopies such as photoluminescence (PL) and absorption spectroscopy have been used to measure the optical band gap and the energies for optical transition between energy levels but they do not reveal the absolute position of electronic energy levels.4,5 Electron spectroscopies such as scanning tunneling spectroscopy enable us to measure the position of electronic energy levels but this method can be applied only to bare nanocrystals since the probe tip should be very close to the nanocrystals to obtain a sufficiently high tunneling current.6,7

Recently, silicon nanocrystals embedded in inorganic or organic insulating films have been widely studied because of their potential for various silicon nanodevices.8,9 The approaches based on scanning tunneling spectroscopy, however, are hampered by the low conductivity of insulating films.10 Furthermore, the electronic structure of nanocrystals is strongly affected by surrounding passivation materials.11 Thus, an appropriate measurement method is required for electronic energy levels of silicon nanocrystals confined in various insulating materials.

Conventional capacitance spectroscopy has been used to probe electronic energy levels of semiconductor quantum dots buried in a wider-gap semiconductor such as InAs quantum dots embedded in GaAs.12 This spectroscopy is applicable only when the tunneling resistance is low, that is, the tunneling current can easily flow in and out the quantum dots through a tunneling barrier. However, the conventional capacitance spectroscopy has difficulties in applying to semiconductor nanocrystals buried in an insulating material such as silicon nanocrystals in silicon oxide or silicon nitride because of the high tunneling resistance of the insulating material. Here, we introduce a capacitance spectroscopy modified for the measurement of absolute position of the lowest conduction and the highest valence levels of the silicon nanocrystals buried in highly resistive insulating films. The modified capacitance spectroscopy makes use of a forced injection of charge carriers into the silicon nanocrystals under a dc bias, and identifies the electronic energy level of the silicon nanocrystals by capacitively detecting the strongly localized charges, whereas, in the conventional capacitance spectroscopy, the charging and discharging of quantum dots along with an ac bias make a differential capacitance peak corresponding to the electronic energy level.

In this study, we focused on the identification of absolute position of electronic energy levels by measuring the charging characteristics of quantum-confined silicon nanocrystals. In order to accomplish this aim, we fabricated a tunneling capacitor device, which contained silicon nanocrystals. Figure 1(a) shows a schematic of the devices which consist of

![Image](a) Schematic of fabricated devices with silicon nanocrystals. (b) Cross-sectional TEM image of a device showing the array of silicon nanocrystals between the tunneling and the blocking silicon nitride layers. The dotted line shows the boundary between the tunneling silicon nitride and the p-Si (100) substrate. (c) Plan-view TEM image of the silicon nanocrystals. The diameter was estimated to be 5.0 nm. (d) Schematic band diagram of the device in flat-band condition.
silicon nanocrystals embedded in a silicon nitride layer, tunneling and blocking silicon nitride layers, and metal electrodes. Trilayer films of a tunneling silicon nitride, an array of silicon nanocrystals embedded in a silicon nitride, and a blocking silicon nitride were grown on p-type (100) Si substrates with a carrier concentration of $9 \times 10^{15}$ cm$^{-3}$ at a temperature of 300 °C in a plasma-enhanced chemical vapor deposition system. The growth of silicon nanocrystal and silicon nitride films is described elsewhere.\textsuperscript{13} Photolithography was used to define top gate electrodes with a size of $50 \times 50$ μm$^2$, followed by electron beam evaporation of 100-nm-thick Al as a top gate and 100-nm-thick Au as a bottom electrode. Figure 1(b) shows a cross-sectional transmission electron microscopy (TEM) image of an array of silicon nanocrystals formed between the tunneling and the blocking silicon nitride layers. The thickness of the tunneling silicon nitride and blocking silicon nitride was measured to be 5.8 nm and 17.2 nm, respectively. Plan-view TEM analysis revealed that the average diameter of the silicon nanocrystals used in the tunneling capacitor device was 5.0 nm, and the standard deviation of Gaussian size distribution was 0.9 nm, as shown in Fig. 1(c). Figure 1(d) shows the energy band diagram corresponding to the fabricated tunneling capacitor device.

The capacitance spectroscopy in the present work consists of two steps. The first step is an injection of charge into the electronic energy levels of silicon nanocrystals. In order to assure that carriers are injected into the silicon nanocrystals through the highly resistive tunnel barrier, a dc bias of injection voltage ($V_{\text{INJ}}$) is applied for a long time scale that guarantees the tunneling through the highly resistive barrier. The second step is the detection of injected charges that are strongly localized in the nanocrystals. The injected carriers are identified from a hysteresis of high frequency (1 MHz) capacitance−voltage (C−V) characteristics. This cycle with the two steps is repeated as a function of $V_{\text{INJ}}$ to produce an injected charge−voltage spectrum, as shown in Fig. 2(b).

To obtain the absolute values of the lowest conduction and highest valence levels of silicon nanocrystals, we measured $\Delta E_C$ and $\Delta E_V$, where $\Delta E_C$ and $\Delta E_V$ are the quantum confinement energies of the silicon nanocrystal in the conduction and valence levels, respectively, as shown in Fig. 1(d). In this study, $\Delta E_C$ and $\Delta E_V$ were extracted from the threshold voltage ($V_{\text{TH}}$) at which a significant charging begins to occur for electron and hole injections, respectively. To measure $V_{\text{TH}}$ for carrier charging, the capacitance spectroscopic measurement was performed on the tunneling capacitor device. Figure 2(a) shows the C−V curves for the device with a silicon nanocrystal diameter of 5.0 nm. A bias stress of $V_{\text{INJ}}$ for 1 s was applied on the top metal gate electrode, and then the gate bias was swept to monitor charging behavior. The appropriate injection time of 1 s was determined by measuring the injected carriers as a function of injection time.\textsuperscript{13} As the C−V curves in Fig. 2(a) show, electrons that are injected and stored in the silicon nanocrystals shift the flat-band voltage ($V_{\text{FB}}$) to the positive bias side, while holes shift $V_{\text{FB}}$ to the negative bias side.\textsuperscript{14} Figure 2(a) also shows that the flat-band voltage shift ($\Delta V_{\text{FB}}$), which is linearly proportional to the stored charge in the silicon nanocrystals,\textsuperscript{15} increases with increasing $V_{\text{INJ}}$. In contrast to the conventional capacitance spectroscopy,\textsuperscript{16} a fingerprint of quantum Coulomb charging would not be seen in the accumulation-inversion transition region of C−V curve because the charge does not transfer through the highly resistive tunneling barrier during the C−V sweep. The measured $\Delta V_{\text{FB}}$ as a function of $V_{\text{INJ}}$ is shown in Fig. 2(b). The $V_{\text{TH}}$ was determined by a linear extrapolation of $\Delta V_{\text{FB}}$ versus $V_{\text{INJ}}$ data. Although the silicon nanocrystals have a size distribution, our model calculation confirmed that the linear extrapolation gives a good approximation to the $V_{\text{TH}}$ of average-sized silicon nanocrystals. At $V_{\text{INJ}}=V_{\text{TH}}$, the lowest conduction (highest valence) level of the silicon nanocrystal coincides with the conduction (valence) band edge of the silicon substrate, and electrons (holes) start to tunnel from the silicon substrate into the silicon nanocrystal by overcoming the $\Delta E_C$ ($\Delta E_V$). Thus, $V_{\text{TH}}$ is a characteristic of the device that reflects the electronic energy level of quantum-confined silicon nanocrystals. The measured $V_{\text{TH}}$ for electron injection was 1.97 V, while that for hole injection was −2.18 V for the device with a silicon nanocrystal diameter of 5.0 nm.

We next focus on the extraction of $\Delta E_C$ and $\Delta E_V$ from the measured $V_{\text{TH}}$’s for electron and hole injections, respectively. $\Delta E_C$/$e$ and $\Delta E_V$/$e$, where $e$ is the elementary charge, are approximately equal to the potential drops across the nanocrystal ($V_{\text{SINC}}$) at $V_{\text{INJ}}=V_{\text{TH}}$. The $V_{\text{SINC}}$ under bias can be estimated based on the numerical calculation of three-dimensional Poisson’s equation as follows:\textsuperscript{16}

$$V_{\text{SINC}} = \frac{d}{t_{\text{blocking}} + \frac{t_{\text{tunneling}}}{\varepsilon_{\text{Si}}}} \times \frac{1}{\varepsilon_{\text{Si}}} \times \left(1.806 - 0.0241 \times d\right) \times V_{\text{SN}}. \tag{1}$$

where $d$, $t_{\text{blocking}}$, and $t_{\text{tunneling}}$ are the diameter of the silicon nanocrystal, thickness of the blocking silicon nitride, and thickness of the tunneling silicon nitride in nanometers, respectively; $\varepsilon_{\text{Si}}$ and $\varepsilon_{\text{SN}}$ are the relative permittivities of the bulk crystalline silicon (11.9) and silicon nitride (6.4), respectively; 1.806 and 0.0241 nm$^{-1}$ are the fitted parameters; and $V_{\text{SN}}$ is the potential drop across the total gate dielectric layer that consists of the tunneling silicon nitride, silicon nanocrystals, and blocking silicon nitride layers. In metal-
insulator-semiconductor systems, the \( V_{SN} \) is given by 
\[
V_{SN} = V_{INJ} - V_{FB} - \psi_S \tag{1}
\]
where \( V_{FB} \) is \(-1.31\) V for the device; and \( \psi_S \) is the potential drop in the silicon substrate.\(^{17}\) The value of \( V_{FB} \) was determined by \textit{C-V} method.\(^{17}\) \( V_{SN} \) and \( \psi_S \) as a function of \( V_{INJ} \) were obtained by solving well-known Poisson’s equation in the metal-insulator-semiconductor structure.\(^{17,18}\) Finally, \( V_{SN} \) as a function of \( V_{SN} \) was obtained from Eq. (1). Figure 3(a) shows the calculated \( V_{SN} \) as a function of \( V_{INJ} \). The dashed lines in Fig. 3(a) indicate \( V_{SN} \) corresponding to the measured \( V_{TH} \): \( \Delta E_C \) (\( eV_{SN} \) at \( V_{INJ} = V_{TH} \) for electron injection) of the silicon nanocrystal with the diameter of 5.0 nm was found to be 0.46 eV, whereas \( \Delta E_V \) (\( eV_{SN} \) at \( V_{INJ} = V_{TH} \) for hole injection) was found to be 0.13 eV, as shown in the inset of Fig. 3(a). The measured \( \Delta E_C \) and \( \Delta E_V \) enable us to assign the absolute position of the lowest conduction and highest valence levels of silicon nanocrystals, respectively, while PL or absorption spectroscopy would address the energies of optical transition between energy levels.

To confirm whether the band-gap energy estimated from the electronic energy levels obtained by the capacitance spectroscopy is same as that responsible for optical transitions, we compared the band-gap energies estimated from the capacitance and PL spectroscopies. The band-gap energy of silicon nanocrystals, as shown in Fig. 3(b), was obtained by using the electron-hole Coulombic interaction energy (1.8e\(^2/2\pi\epsilon_S\alpha_d\)),\(^{19}\) the band-gap energy of the silicon nanocrystals with the diameter of 5.0 nm was estimated to be 1.84 eV, which is in good agreement with that of 1.71 eV predicted by the capacitance spectroscopy with a slight discrepancy between the measured values. Taking into account the quantized subband levels in the accumulation and inversion layers of the substrate, \( \Delta E_C \) and \( \Delta E_V \) would not be accurately equal to the \( eV_{SN} \) at \( V_{INJ} = V_{TH} \). The energy difference between the occupied subband levels and the band edges of the silicon substrate is in the order of a few tens of milli-electron-volt for the conduction and valence bands, respectively,\(^{20}\) and therefore \( \Delta E_C \) and \( \Delta E_V \) would be slightly underestimated in the capacitance spectroscopy. However, these results indicate that the electronic structure of silicon nanocrystals embedded in insulating films can be identified by the modified capacitance spectroscopy.

In summary, we identified the electronic structure of silicon nanocrystals quantum-confined in silicon nitride insulating films by using capacitance spectroscopy. The measured quantum confinement energies revealed the absolute position of the lowest conduction and highest valence levels of the silicon nanocrystals quantum-confined in the silicon nitride films. The band-gap energy estimated by the capacitance spectroscopy agrees well with that measured by PL spectroscopy.

We thank Professor Charles W. Tu (University of California, San Diego) for valuable discussions. This work was partially supported by the World Class University program at the Gwangju Institute of Science and Technology through a grant provided by the Ministry of Education, Science and Technology of Korea (Grant No. R31-2008-000-10026-0) and the Korea Science and Engineering Foundation NCRC grant funded by the Korea government (Grant No. R15-2008-006-02001-0).