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The energy band alignment of Si nanocrystals in SiO_2

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The determination of the energy band alignment between the 2.6-nm-diameter Si nanocrystals and the SiO_2 host is achieved by means of photo-ionization/-neutralization and capacitance spectroscopy. The measured conduction and valence band offsets are 2.6 eV and 4.4 eV. The band gap is evaluated to be 1.7 eV by photoluminescence. These results indicate that the valence band offset at the Si nanocrystals/SiO_2 interface is quite close to the one observed at bulk Si/SiO_2 interface. On the contrary, we observe a clear upward shift (0.5 eV) of the conduction band in the Si nanocrystals/SiO_2 system with respect to the bulk Si/SiO_2 hetero-structure. © *2011 American Institute of Physics*. [doi:10.1063/1.3629813]

Si nanocrystals (ncs) embedded in oxide host have been intensively studied both to investigate the properties of the matter at nanometric scale and for nanoelectronic, optoelectronic, and photovoltaic applications.[1–4] The band gap of Si ncs increases when their size shrinks. Several theoretical works described this issue[5] and different optical techniques as photoluminescence (PL), spectroscopic ellissometry, and optical absorption have been used to prove this fact.[6–8] On the other hand, in the perspective of the technological applications, a lot of works has been carried out on the electrical characteristics, in particular related to the charge trapping properties of the Si ncs based metal-oxide-semiconductor (MOS) structures.[9] Among these wide characterization efforts, the direct measurement of the Si ncs energy alignment in the SiO_2 host is still lacking. The present work is focused on the experimental determination of the energy band alignment of Si ncs in a SiO_2 matrix. This goal is achieved through the measurement of their conduction band (CB) and valence band (VB) energy positions in the SiO_2 host compared to the bulk Si/SiO_2 interface energy barriers.

The band alignment at the bulk Si/oxide interface is usually characterized by means of internal photoemission or x-ray photoelectron spectroscopy.[10–15] Differently, in the case of the Si ncs embedded in a SiO_2 matrix, these techniques are not reliable, due to the overlap of the signals of the Si ncs with those of the Si/SiO_2 interface. Therefore, in order to single out the effects due to the Si ncs, the variations of the charging state of the Si ncs upon different, electrical or optical, stress were addressed as a key property to investigate the Si ncs band alignment. We integrate the information obtained by PL on the Si ncs average band gap with the measurements of the VB shift (ΔVB) obtained by photo-ionization (PI)[16,17] and those of the CB shift (ΔCB) measured by photo-neutralization (PN)[16,17] and capacitance spectroscopy (C-S).[18] The overall results allow obtaining a consistent description of the energy band alignment of Si ncs in SiO_2.

SiO_2/SiO/SiO_2 multilayer structures were fabricated by subsequent SiO and SiO_2 depositions in an electron-beam evaporation system without breaking the high vacuum (base pressure 5×10^{-7} mbar) regime to avoid interfaces contamination. A 6-nm-thick SiO layer was deposited between a 3-nm-thick SiO_2 layer, tunnel oxide (TO) and a 10-nm-thick SiO_2 layer, blocking oxide (BO). Prior to the deposition all the n-type, 1-5 Ω cm, Si (100) substrates were dipped in HF solution to obtain a clean surface. A 15-nm-thick SiO_2 reference sample was deposited without any SiO interlayer. To promote the formation of the Si ncs, all the samples were annealed in a conventional quartz-tube furnace at 1050 °C for 1800 s in a N_2 flux.[9,19] Finally, all the samples were annealed in forming gas, H_2:N_2, for 900 s at 400 °C in a rapid thermal processing machine. MOS capacitors were fabricated by thermally evaporating semitransparent Al (15-nm-thick) circular electrodes (0.08 mm^2 area) through a shadow mask as the top gate and 100-nm-thick Al as the bottom electrode.

The Si ncs formation in the SiO_2 host was investigated by means of high resolution electron microscopy and energy filtered transmission electron microscopy.[20] These measurements corroborated the full crystalline character of the Si nanoclusters and provided the thickness of the stack after the thermal treatment. The SiO_2 TO and BO were determined to be 5.3 ± 0.3 nm and 10.9 ± 0.5 nm thick, respectively. The mean diameter of the Si ncs was 2.6 ± 0.1 nm. The average ncs density is in the order of 10^{11}-10^{12} cm^{-2}.[9] The evaluation of the Si ncs average band gap was achieved by PL. The spectra were acquired using an Ar laser for excitation ($\lambda = 488$ nm). A strong emission band peaked around 1.45 ± 0.05 eV was found, in agreement with data reported in the literature.[7,8,19] As noticed by Garrido *et al.*,[7] the emission energy is affected by a Stokes shift of 0.26 ± 0.03 eV with respect to the absorption energy irrespective of the size of the Si ncs. Taking in account this effect, the optical band gap of the Si ncs embedded in SiO_2 matrix was evaluated to be 1.7 ± 0.1 eV.

Both PI/PN and C-S measurements capacitively detect the localized charges in the Si ncs by monitoring the shift of the flat band voltage (V_{FB}) in capacitance-voltage (CV) curves. The CV curves were acquired sweeping the applied voltage between inversion to accumulation at 100 KHz in a dark environment in a shielded probe station. A 150 W Xe arc lamp was used as the radiation source for PI/PN measurements. The photon spectral range was $h\upsilon = 2.0$-6.0 eV while

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the incident photon flux (n_{ph}) was measured using a Si photodiode.[11]

During PI measurements (Fig. 1, inset), the transition of the Si ncs from the neutral to the positive state was caused by an optical excitation of the electrons from the Si ncs VB to the SiO_2 CB. The samples were illuminated with monochromatic photons for $\Delta t = 300$ s with a positive applied voltage ($V = +1.5$ V) to collect the excited electrons at the metal gate. Subsequently, a CV curve was acquired in darkness to measure the V_{FB} position. This procedure was repeated at different photon energy values ranging from 2.0 to 6.0 eV with step of 0.1 eV to monitor the V_{FB} evolution as function of the photon energy. The same analysis was performed during PN measurements (Fig. 2, inset) on Si ncs that were preliminarily charged by electrons tunnelling through the SiO_2 potential barrier from the substrate, applying a suitable dc bias (+9 V, 5 s). In this case, the monochromatic light irradiation induced the transition of the Si ncs from the initial negative state to a neutral state, due to the optical excitation of electrons from the Si ncs CB to the SiO_2 CB.

From the shift of the V_{FB} with respect to the initial state (ΔV_{FB}), we determined the charge variation $\Delta V_{FB} * C_{OX}$ (where C_{OX} is the capacitance of the device per cm^2) in the Si ncs as a function of $h\nu$. Normalizing on the number of incident photon $n_{ph} * \Delta t$, we calculated the relative quantum yield (Y) which is defined as

$$Y = \frac{\Delta V_{FB} * C_{OX}}{n_{ph} * \Delta t}. \quad (1)$$

The extrapolation of $Y^{1/2}$ to zero yield allows the determination of the different barrier energies during ionization and neutralization processes.[16,17]

In Fig. 1 (left axis), the V_{FB} evolution during PI measurements is reported. The V_{FB} shifts towards negative values for photon energies above ~4 eV, indicating that, above this threshold, negative charges are extracted from the Si ncs. The extrapolation of the calculated $Y^{1/2}$ to zero yield is depicted in Fig. 1 (right axis). The barrier energy for the ionization process, from the Si ncs VB to the SiO_2 CB, was found to be 4.5 ± 0.1 eV. By considering a SiO_2 band gap of 8.9 ± 0.1 eV, the VB offset between the Si ncs and the SiO_2 results to be 4.4 ± 0.1 eV. The magnitude of the energy transition corresponding to the ionization process at the bulk Si/

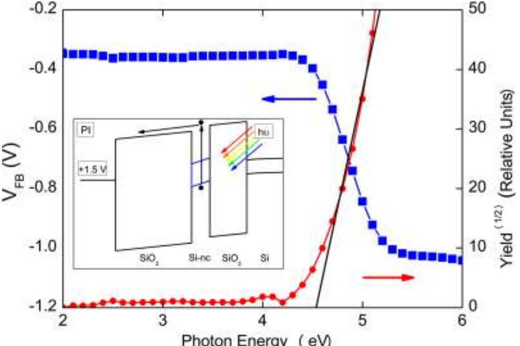

FIG. 1. (Color online) (Left, blue square) V_{FB} as function of the photon energy for Si ncs MOS based device after different monochromatic photon energy irradiation (from 2.0 eV to 6.0 eV, step 0.1 eV) for 300 s under positive (+1.5 V) bias. (Right, red circle) $Y^{1/2}$ as function of the photon energy for the same process. (Inset) Band diagram of the PI transition involved.

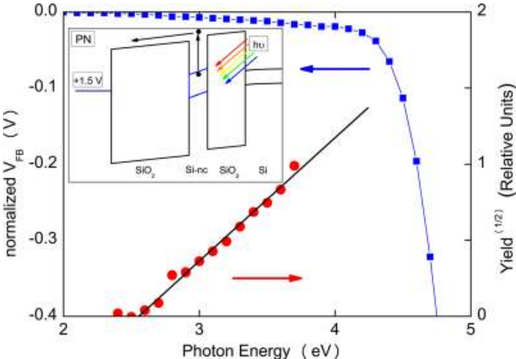

FIG. 2. (Color online) (Left, blue square) Normalized V_{FB} as function of the photon energy for PN spectra of previously charged (+9 V, 5 s) Si ncs MOS based device after different monochromatic photon energy irradiation (from 2.0 eV to 6.0 eV, step 0.1 eV) for 300 s under positive (+1.5 V) bias. (Right, red circle) $Y^{1/2}$ versus incident photon energy for the same process. (Inset) Band diagram of the PN transitions involved.

SiO_2 interface is 4.3 ± 0.1 eV.[15] The difference among these values results in a ΔVB of 0.2 ± 0.1 eV between the Si ncs embedded in the SiO_2 matrix and the bulk Si substrate.

In Fig. 2 (left axis), the V_{FB} evolution during PN measurements is reported. In order to remove all the artefacts related to the detrapping effects occurring in darkness, the reported V_{FB} values were corrected by the subtraction of the corresponding V_{FB} values acquired under the same experimental condition but without monochromatic light irradiation. As observed in the PI spectra, there is a clear onset in the V_{FB} curve for photon energies above ~4 eV, due to the transition of electrons from the Si ncs VB to the SiO_2 CB. In addition, we observed a clear light induced V_{FB} variation for photon energy below 4 eV. The calculated $Y^{1/2}$ for $h\nu$ values ranging from 2 eV to 4 eV is depicted in Fig. 2 (right axis). By means of the $Y^{1/2}$ extrapolation to zero yield, a barrier energy value of 2.6 ± 0.1 eV was extracted for the neutralization process. This barrier corresponds to the CB offset between the Si ncs and the SiO_2. The CB offset at the bulk Si/SiO_2 interface is 3.1 ± 0.1 eV (Ref. 15) and so the resulting ΔCB value is 0.5 ± 0.1 eV.

The ΔCB was measured by C-S as well. By this technique, electrons were electrically injected in the Si ncs by means of a positive dc bias (V_{INJ}) applied to the metal gate for 1 s.[18] When the V_{INJ} is high enough, the lowest CB level of the Si ncs coincides with the CB of the Si substrate and electrons start to tunnel from the Si substrate into the Si ncs through the SiO_2 potential barrier. The trapping of negative charges in the Si ncs results in a positive shift of the V_{FB}. In the inset of Fig. 3, we report the C-V curves acquired at different V_{INJ} values in the 1-9 V range with steps of 1 V. A rigid shift of the C-V curves is observed for V_{INJ} values above 5 V due to the injection of negative charges in the Si ncs. In Fig. 3, we reported the evolution of the V_{FB} as a function of V_{INJ}. From this curve, the threshold voltage (V_{TH}) at which a sizeable charging begins to occur was determined by linear extrapolation. The V_{TH} was found to be 5.85 ± 0.05 V.

As reported by Cho *et al.*,[18] the value of $\Delta CB/e$, where e is the elementary charge, corresponds to the potential drop across the Si ncs (V_{nc}) at $V_{INJ} = V_{TH}$. V_{nc} can be defined as

$$V_{nc} = df * V_{OX}. \quad (2)$$

The dielectric factor (df)[21] is given by

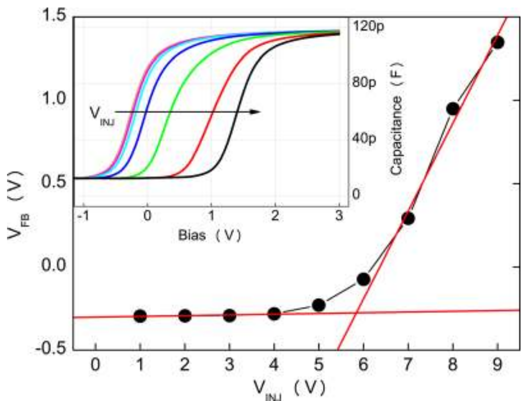

FIG. 3. (Color online) V_{FB} as function of the V_{INJ}. (Inset) CV characteristic of Si ncs MOS based device after charging achieved by different applied V_{INJ} before the sweep (from 1 V to 9 V, step 1 V, 1 s).

$$df = \frac{\frac{d}{\varepsilon_{Si}}}{\frac{t_{BO}}{\varepsilon_{BO}} + \frac{d}{\varepsilon_{Si}} + \frac{t_{TO}}{\varepsilon_{TO}}} * (1.806 - 0.0241 * d), \quad (3)$$

where d, t_{BO}, and t_{TO} are the diameter of Si nc, the thickness of the BO, and of the TO in nanometers, respectively; ε_{Si}, ε_{BO}, and ε_{TO} are the relative permittivity of the Si (11.9) and of the BO and TO (3.9), respectively. V_{OX} is defined as the potential drop across the total dielectric between the Si substrate and the metal gate that is given by

$$V_{OX} = V_{INJ} - V_{FB} - \psi_S, \quad (4)$$

where ψ_S is the potential drop across the Si substrate which is obtained by solving Poisson's equations at $V_{INJ} = V_{TH}$.[22,23] According to this model, the above reported V_{TH} value results in a ΔCB of 0.5 ± 0.1 eV, in perfect agreement with the PN results.

The same PI/PN and C-S measurements were performed on the annealed 15-nm-thick SiO_2 sample under the same experimental conditions. Interestingly, no detectable V_{FB} shift was observed in this reference sample. Thus, the previously reported V_{FB} variations are unambiguously related to charge trapping/detrapping phenomena occurring in the Si ncs embedded in the SiO_2 matrix.

Figure 4 summarizes the energy band alignment for Si ncs of 2.6 nm of diameter embedded in SiO_2 host. It is interesting to note that the overall gap obtained by adding the evaluated ΔCB (0.5 eV), the ΔVB (0.2 eV), and the bulk Si band gap (1.1 eV) is found to be 1.8 ± 0.1 eV, in excellent agreement, within the experimental errors, with the 1.7 ± 0.1 eV value of the band gap measured by PL. The band gap value reflects both the strong confinement regime and the surface chemistry effects. Moreover, these experimental data clearly indicate that there is an asymmetric shift of the Si ncs band edges in the SiO_2 matrix host with respect to the bulk Si/SiO_2 interface. In particular, the ΔCB (0.5 eV) is larger than the ΔVB (0.2 eV) as already predicted by different theoretical works.[5,6,24,25]

In conclusion, we have measured the energy band alignment of Si ncs hosted in SiO_2 by combining various standard electro-optical techniques. This achievement paves the way to a systematic investigation of the evolution of band alignment of Si ncs in SiO_2 as a function of Si ncs band gap by properly tuning their dimensions.

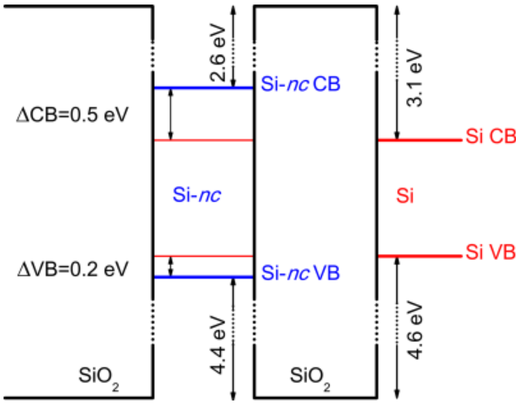

FIG. 4. (Color online) Band diagrams of the 2.6 nm diameter Si ncs embedded in SiO_2 according to the data measured by means of C-S, PI/PN, and PL.

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