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Effects of surface ligands on the charge memory characteristics of CdSe/ZnS nanocrystals in TiO₂ thin film

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Charge memory characteristics have been systematically studied based on colloidal CdSe/ZnS nanocrystal quantum dots (QDs) embedded in ~50 nm-thick TiO₂ film. Ligand-capped QDs showed negligible electron charging effect, implying that the electron affinity of QDs was significantly decreased by surface dipole layer surrounding QDs. In contrast, the hole charging was affected by the carrier injection blocking effect of the surface ligands. Efficient electron and hole charging characteristics were realized by removing the surface ligands via H₂ plasma treatment. © 2009 American Institute of Physics. [doi:10.1063/1.3259929]

Semiconductor nanocrystal quantum dots (QDs) synthesized by colloidal solution chemistry have attracted extensive attention for their electronic and optoelectronic device applications such as memories[1–3] and light-emitting diodes.[4,5] Nanocrystal nonvolatile memories can be one of the promising applications exploring the full potential of the zero-dimensional system of colloidal QDs.[1–3] Colloidal QDs have enormous advantages such as chemical flexibility and size and shape tunability.[1] Semiconductor nanocrystals such as CdSe/ZnS QDs also show charge storage effects as well as high quantum efficiency so that they can be applied for both electrically and optically induced charge memories. Recently, charge memory effects have been reported in CdSe QDs hybridized in a soft-material (e.g., polymer) matrix.[2,3] However, little information is available on the charge storage characteristics of nanocrystal QDs embedded in oxides even though the QD system in oxide is compatible with modern Si technology and more electronically and chemically stable than those in a polymer matrix. Moreover, the effects of surface organic ligands on the charging characteristics of QDs in oxide have not been addressed so far. Carrier injection into QDs can be significantly affected by surface ligands acting as the current blocking layer.[5] In addition, recent QD energy level studies indicate that surface ligands can form a dipole layer at the interface of QDs and ligands.[6,7] Consequently, the electron affinity and electron binding energy levels become smaller than the estimated values based on the bulk energy levels and quantum confinement effects.[4,7,8] In this letter, we report the effects of QD surface ligands on the electron and hole charging characteristics of CdSe/ZnS QDs embedded in a TiO₂ thin film.

The charging characteristics were investigated by using metal-oxide-semiconductor (MOS) structures as seen in Fig. 1(a). The MOS structure was fabricated by spreading QDs on p-type Si substrates via spin coating, followed by capping ~50 nm-thick TiO₂ film. As a matrix, TiO₂ was chosen because of its wide bandgap energy (e.g., ~3.2 eV for anatase

phase), appropriate electron affinity (3.9 eV),[9] excellent optical characteristics, and high dielectric constant. Considering the bandgap energy (1.65 eV) and electron affinity (4.95 eV) of bulk CdSe,[10,11] the offsets of conduction and valence band edges are ~1.05 and 0.5 eV, respectively, [Fig. 1(b)]. The conduction band offset can be decreased to ~0.7 eV due to a quantum confinement effect.[7] This value is smaller than those (3.5 and 1.5 eV, respectively) of Si nanocrystals in SiO₂ and HfO₂.[12] Thus, the TiO₂ tunneling thickness should be thicker in terms of data retention for nonvolatile memory applications. However, the smaller conduction band offset (~0.15 eV) of TiO₂ and Si substrate can reduce the programming (writing) voltage significantly.

Two different kinds of surface ligands were applied for CdSe/ZnS QDs. One was a mixture of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) ligands in which QDs were synthesized. The other was 3-mercaptopropionic acid (MPA) replacing TOPO and HDA in methanol. The MPA ligand has relatively shorter and polar chains, while the TOPO and HDA ligands have longer and nonpolar chains. Thus, the MPA ligand can have an advantage over TOPO/HDA ligands in terms of carrier injection. In addition, the charging characteristics of the QDs were studied as a function of H₂ plasma cleaning processing time at 100 °C. The details of the QD synthesis and H₂ plasma treatment have been described elsewhere.[5] The TiO₂ film was deposited at temperatures of 200 °C over QDs/Si by using titanium tetra
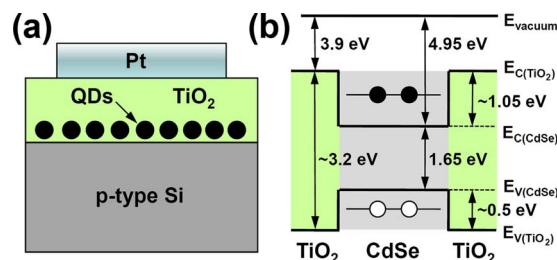

FIG. 1. (Color online) (a) Schematic of the MOS structure with nanocrystal QDs embedded in a TiO₂ thin film and (b) the schematic energy-band diagram of a CdSe QD in TiO₂.

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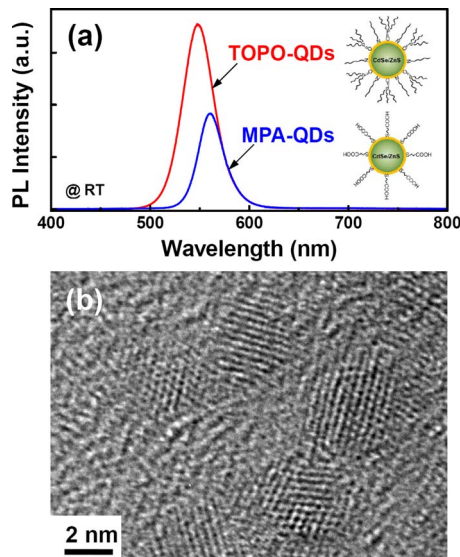
FIG. 2. (Color online) (a) PL spectra of TOPO- and MPA-capped CdSe/ZnS QDs on the Si substrates and (b) the corresponding high-resolution TEM lattice image of the TOPO-capped CdSe/ZnS QDs.

isopropoxide $[Ti(OiC_3H_7)_4]$ bubbled with an Ar flow of 50 SCCM (SCCM denotes cubic centimeter per minute at STP) at 30 °C. The rf plasma power, chamber pressure, O_2 flow rate, and total gas flow rate were fixed at 50 W, 1.2 Torr, 50 SCCM, and 200 SCCM, respectively. Finally, a 0.1 μm-thick Pt metal film with a diameter of 200 μm was deposited on TiO_2 by sputtering for the capacitance-voltage (C-V) characterization in series mode.

Figure 2(a) shows the photoluminescence (PL) (a 325 nm helium-cadmium laser excitation) spectra of TOPO- and MPA-QDs on the Si substrates. The TOPO-QDs shows a good PL spectrum peaked at ~550 nm with high PL efficiency. The PL peak of the MPA-QDs was slightly redshifted to ~560 nm with respect to that of the TOPO-QDs. This may be due to the less potential confinement effect of shorter chains and the different surface dipole effect of MPA. The corresponding transmission electron microscopy (TEM) study revealed that the QDs had an average size of ~5 nm as seen in Fig. 2(b).

Figure 3 shows the high-frequency (1 MHz) C-V characteristics of the MOS structures possessing TOPO- and MPA-QDs, as well as a TiO_2 film without QDs (referred to here as reference TiO_2). The voltage of the top electrode was swept from −3 to +3 V and back to −3 V. The TOPO- and
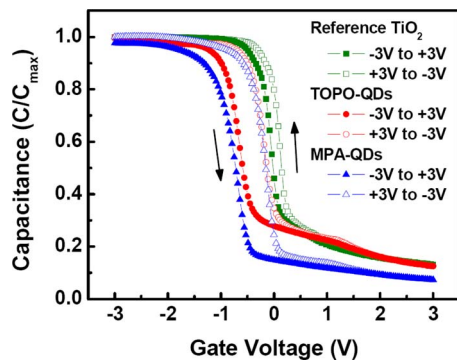

FIG. 3. (Color online) C-V hysteresis characteristics of the reference TiO_2 and TOPO- and MPA-QD samples.
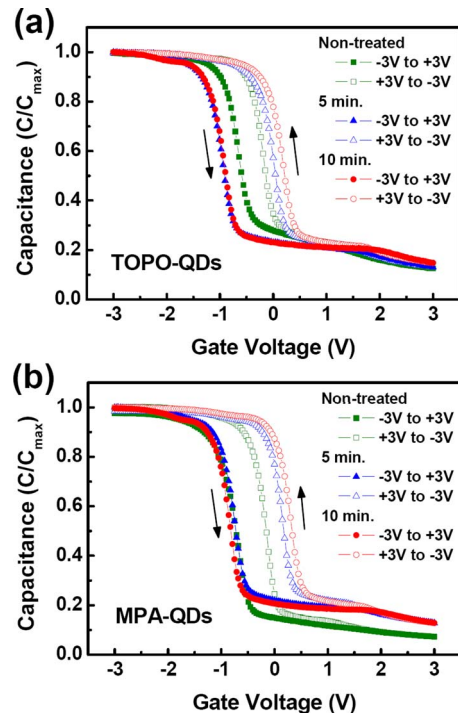

FIG. 4. (Color online) C-V hysteresis characteristics of (a) the TOPO- and (b) MPA-QD samples treated by H_2 plasma for 5 and 10 min along with the nontreated QD samples.

MPA-QD samples show the significant C-V hysteresis widths (ΔV_{FB}) of 0.46 and 0.61 V, respectively, while the reference TiO_2 has the small C-V hysteresis width of 0.05 V. As explained later, the QDs in TiO_2 can be the main origin of the obtained hysteresis results even though the effects of the organic ligands cannot be completely ruled out. We note that all of the samples studied here possess counterclockwise C-V hysteresis loops, indicating that the hysteresis can be due to the charge transfer between the QDs and a Si substrate via a tunneling.[13] As expected, the flatband voltages of the QD samples are shifted to the negative voltages with respect to that of the reference TiO_2 for the sweep from −3 to +3 V because of the hole charging effect. However, the flatband voltage shifts of the QD samples are also negative values for the sweep from +3 to −3 V.

To further gain insight into the QD charging characteristics, systematic C-V studies on the MOS structures possessing H_2-plasma-treated QDs were carried out. Our previous study revealed that the H_2 plasma treatment was very effective in enhancing the carrier injection and electroluminescence (EL) of the QDs.[5] As seen in Fig. 4, the C-V hysteresis width becomes larger with increased H_2 plasma treatment time. Interestingly, the increased widths are mainly due to the positive flatband voltage shifts in the sweep from +3 to −3 V, except for the TOPO-QD sample treated for 5 min. As compared to the nontreated QD sample, the TOPO-QD sample treated for 5 min possesses the flatband voltage shifts of −0.32 and 0.17 V in the sweeps from −3 to +3 V and +3 to −3 V, respectively [Fig. 4(a)]. When the treatment time is increased to 10 min, the flatband voltage is further shifted to a positive voltage in the sweep from +3 to −3 V, while this is not changed in the sweep from −3 to +3 V. A similar behavior of the C-V characteristics is observed in the MPA-QD samples as seen in Fig. 4(b). The increased C-V hysteresis widths of the H_2-plasma-treated QD samples re-

sult from the positive flatband voltage shifts in the sweep from +3 to −3 V. In contrast, the flatband voltage shifts of the sweep from −3 to +3 V are essentially unchanged regardless of the removal of the surface ligands by H_2 plasma treatment.

The C-V results can be understood in terms of the impact of a surface dipole layer at the interface of the QDs and organic ligands. A surface dipole layer surrounding the QDs can be formed by the polar bonds between the QDs and the organic ligands.[6,7] Campbell *et al.*[7] reported that the surface dipole pointing radially outward decreases the electron affinity of the HDA-capped CdSe/ZnS QDs by 0.7 eV. With added quantum confinement effect (∼0.35 eV), the electron accepting level was 3.9 eV.[7] The electron affinity level is consistent with other electrochemical studies on CdSe QDs.[4,8] Therefore, ligand-capped CdSe/ZnS QDs are unable to store electrons in TiO_2 since the electron affinity of TiO_2 is 3.9 eV. It is confirmed by the result that the electron charging effect is not pronounced in the C-V measurements of the TOPO- and MPA-QD samples (Fig. 3). When the ligands are removed by H_2 plasma treatment, the surface dipole effect is diminished. Consequently, the flatband voltages become gradually shifted to the positive voltage by the electron charging effect in the sweep from +3 to −3 V with increased H_2 plasma treatment time (Fig. 4).

Meanwhile, the hole charging in QDs seems to be affected by the carrier injection blocking effect rather than by the increased ionization potential of the organic ligands. TOPO and HDA can yield a worse carrier injection efficiency than MPA because of their longer and nonpolar chains.[5] As a result, the TOPO-QD sample shows a smaller flatband voltage shift (−0.61 V, with the respect to that of reference TiO_2) in the sweep from −3 to +3 V than the MPA-QD sample (−0.78 V) as seen in Fig. 3. Note that the flatband voltage shift of the TOPO-QD sample is further increased by −0.93 V when treated by H_2 plasma for 5 min [Fig. 4(a)]. In contrast, the MPA-QD samples show the almost same flatband voltages in the sweep from −3 to +3 V regardless of H_2 plasma treatment [Fig. 4(b)]. The results are consistent with our recent EL study on the same QD system.[5] With the H_2 plasma treatment time increased to 10 min, the TOPO- and MPA-QD samples eventually show the saturated C-V hysteresis widths of 1.11 and 1.16 V, respectively, which are limited by the total number of QDs in TiO_2.

In conclusion, we demonstrated the charge memory characteristics of colloidal CdSe/ZnS QDs embedded in a TiO_2 thin film. Electron charging was negligible for both TOPO and MPA-QDs since the electron affinity of QDs could be significantly decreased to the level of TiO_2 due to the surface dipole effect of ligands/QDs. In contrast, the hole charging was affected by the carrier injection blocking effect of the surface ligands, where the MPA-QDs had an advantage over the TOPO-QDs. When the surface ligands were removed by H_2 plasma, both electron and hole charging characteristics were fully utilized. The results open another path for the application of various colloidal nanocrystal QDs for promising large-area Si-based nanocrystal memory devices.

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