Electron charging and discharging in amorphous silicon quantum dots embedded in silicon nitride

Nae-Man Park  
Basic Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon 305-350, Korea

Suk-Ho Choi  
College of Electronics and Information and Institute of Natural Sciences, Kyung Hee University, Suwon 449-701, Korea

Seong-Ju Park a)  
Department of Materials Science and Engineering and Center for Optoelectronic Materials Research, Kwangju Institute of Science and Technology, Kwangju 500-712, Korea

(Received 28 January 2002; accepted for publication 3 June 2002)

Electron charging and discharging were produced in metal-insulator-semiconductor structures containing amorphous silicon quantum dots (a-Si QDs) by increasing the applied voltage in a stepwise fashion without changing its sign. The metal-insulator-semiconductor structure was fabricated using an insulating silicon nitride film containing a-Si QDs by plasma-enhanced chemical vapor deposition. This charging behavior suggests that a-Si QDs in the silicon nitride are positively charged due to nitrogen dangling bonds. The surface state of the a-Si QDs is considered to play a dominant role in the charging properties such as electron storage and charge-loss rate in the a-Si QDs. © 2002 American Institute of Physics. [DOI: 10.1063/1.1497444]

Silicon nanostructures are currently the subject of intensive study in terms of their applications in optoelectronic devices 1–3 because optical transitions in such systems are direct in nature and their rates are very high compared with bulk silicon. Silicon nanostructures may also be used as quantum electronic devices such as single electron transistors, switching devices, and memory devices. 4 Recently, several research groups have investigated charge storage effects in silicon nanostructures and reported on their potential applications to memory devices. 5–8 Silicon-based nm-size flash-memory devices have characteristics that include long-term charge storage, fast response, and low power requirement. 5,7,9 However, these devices are sensitive to the requirements such as electron storage and charge-loss rate in the a-Si QDs.

The thickness of the nitride film was 45 nm and the average size of the embedded a-Si QDs was 1.3–1.4 nm. MIS structures were fabricated by depositing an 80-nm-thick Al layer through a mask of 30 × 30 μm² onto both the top of silicon nitride films and the backside of the silicon substrates by means of an e-beam evaporator. Capacitance–voltage (C–V) characteristics were measured with an HP 4284A precision LCR meter at 1 MHz. Fourier transform infrared (FTIR) and photoluminescence (PL) spectroscopy were also employed to characterize the chemical bonding configurations as well as the optical properties of a-Si QDs. FTIR spectra were obtained by scanning the range of wave numbers from 500 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. A charged coupled device detector was used for the PL measurement at room temperature and a He–Cd 325 nm laser was used as the excitation source. The a-Si QD MIS structures used in this study showed two different charging effects and, as a result, the samples were classified into two groups, referred to as groups A and B. Group-A samples were grown using a plasma power of 6 W and group-B samples were grown using a slightly lower plasma power of 5 W. The mean sizes of a-Si QDs grown under these growth conditions were not changed but the surface states of a-Si QDs were influenced by changes in the plasma power as described below.

Figure 1 shows a comparison of typical C–V hysteresis curves for a group-A sample with those for a group-B sample. No hysteresis curves are found in the small range of voltage sweep; (−5, +1) V for the group-A sample and (−10, −2) V for the group-B sample, respectively, as shown in Figs. 1(a) and 1(b). However, a considerable C–V hysteresis was observed when the voltage sweep range was increased for both samples. In the case of group A, the magnitude of the hysteresis reaches ~4.3 V in the sweep range (~20, +16) V. It should also be noted that the shift of C–V...
curve with respect to the curve with no hysteresis is clearly larger for a sweep of \(-V\rightarrow +V\) (hole charging) than for a sweep of \(+V\rightarrow -V\) (electron charging). This appears to be caused by the larger shift of the energy level in the conduction band than that in the valence band by a quantum confinement effect,\(^{11}\) thus lowering the tunneling barrier for electrons in the \(a\)-Si QDs compared to that for holes. As a result, electrons can escape from the \(a\)-Si QDs more easily than holes, resulting in a smaller \(C-V\) shift by electron charging.

In Fig. 1(b), the group-B sample shows very different charging behaviors. A shift in the \(C-V\) curve is observed only during a sweep of \(+V\rightarrow -V\), but no shift is detectable in the opposite direction as shown in the inset. The \(C-V\) curve is shifted towards positive voltages by increasing the upper boundary of the sweep range to 8 V, and is then shifted towards the opposite direction, i.e., towards negative voltages for sweep voltages larger than 8 V. This charging/discharging effect has not been previously observed.

To explain the observed charging/discharging effects as shown in Fig. 1(b), it is assumed that the \(a\)-Si QDs in the silicon nitride layer are positively charged. This assumption is supported by the result that the \(C-V\) curves with no hysteresis shift towards negative voltages with respect to the ideal \(C-V\) curve as shown in Fig. 1.\(^{12}\) In addition, it has also been shown that silicon nanocrystals can be positively charged.\(^8\) The shifts in \(C-V\) curves with no hysteresis from the ideal \(C-V\) curves are \(-1.64\) V and \(-3.81\) V for the group A and B samples, respectively. Therefore, more QDs are assumed to be positively charged in the group-B sample than in the group-A sample. This makes it difficult for extra hole charging to occur during a sweep of \(-V\rightarrow +V\) in the group-B sample, resulting in the absence of shift in the \(C-V\) curve during a sweep of \(-V\rightarrow +V\) in the group-B sample as shown in the inset of Fig. 1(b). When the upper boundary of the voltage sweep range is increased, some of the positively charged \(a\)-Si QDs are neutralized by trapping electrons injected from the accumulation layer in the Si wafer during a sweep of \(+V\rightarrow -V\). This causes a shift in the \(C-V\) curve towards positive voltages. However, when the upper boundary of the voltage sweep range is further increased, trapped electrons in the \(a\)-Si QDs can be transferred towards the top metal layer by the strong electric field. Some of the neutral \(a\)-Si QDs near the Si wafer are then positively charged by the remaining holes. If the hole charging caused by this effect is larger than electron charging caused by the injection of electrons from the Si wafer, a shift in the \(C-V\) curve towards negative voltages can be observed, as shown in Fig. 1(b).

These findings can be used to design a new functional memory device because charging/discharging states can be achieved only by incrementing the voltage in a stepwise manner without changing its sign.

The charging effects in conventional MIS structures without QDs in the insulator are usually attributed to two types of defects such as a bulk trap in the insulator and an interface trap between the insulator and semiconductor.\(^{13}\) It has previously been shown that charging effects due to interface traps in such MIS structures occur even in the small sweep range of \(6\) V,\(^{14}\) and are independent of sweep range.\(^ {10}\) For simplicity, interface traps were neglected in this discussion because the silicon nitride/Si interface states would be expected to be low, judging from the absence of hysteresis in the \(C-V\) curve in the small range of voltage sweep, as shown in Figs. 1(a) and 1(b).

PL measurements were employed to further investigate the charging properties of group A and B samples. The PL intensity of a typical group-A sample is merely 4 times stronger than that of a group-B sample, as shown in Fig. 2. This can be attributed to a lower QD density and/or a larger bulk trap density in the group-B samples. Based on the data in Fig. 1, the hysteresis in the \(C-V\) curves for electron charging are \(1.4\) and \(1.6\) V for both groups, respectively; indicating that the number of electrons charged in \(a\)-Si QDs is similar for both samples. Therefore, the entire charge-trap
(QDs and bulk traps) density of the group-B samples is believed to be almost same as that of the group-A samples. This result indicates that group-B samples have a lower QD density and larger bulk trap density compared to group-A samples, which shows a weak luminescence.

These results were also confirmed by FTIR spectral data on the samples. Figure 3(a) shows that amorphous silicon nitride and a-Si films grown by PECVD show Si–N, Si–H, and Si–Si vibrational modes in the wave number range from 800 to 1050 cm$^{-1}$ and these peaks are also observed in a-Si QD samples as shown in Fig. 3(b). In the case of a group-A sample, however, an additional peak is observed at about 3350 cm$^{-1}$ which corresponds to a N–H bond. The N–H bonding mode at 3350 cm$^{-1}$, which is related to the formation of a-Si QDs, was not observed in an amorphous silicon nitride film without a-Si QDs grown by SiH$_4$ and N$_2$ plasma as shown in Fig. 3(a). The N–H bonding, therefore, appears to be formed at the surface of the a-Si QDs and is closely related to the surface states of the a-Si QDs. However, this mode is not seen in Fig. 3(b) for a group-B sample, indicating that nitrogen dangling bonds are not passivated with hydrogen at the surface of the a-Si QDs in a group-B sample. It has been reported that nitrogen dangling bonds could contribute to positively charged defects. This fact is consistent with the above discussion, in which a-Si QDs are positively charged in group-B samples. Because the surface states related to nitrogen dangling bonds at the surface of the a-Si QDs are deep states, most electrons are believed to fill the surface states. The nitrogen dangling bonds, therefore, have a dominant effect on the electron-transfer between QDs and the weak PL of a group-B sample is also related to the surface state of the a-Si QD that plays a major role in the characteristic charging behavior observed here.

The charge-loss rate is another important factor in memory devices. Figure 4 shows a comparison of charge-retention characteristics for a group-A sample with those for a group-B sample, in which the group-B sample shows a larger charge-loss rate. After electrons are injected into a-Si QDs in a group-B sample, their charge density decreases gradually with time, resulting in a drop of 50% in its magnitude at 1000 s, while the charge density of the group-A sample persists at a nearly constant level for 1000 s. A large charge-loss rate due to surface states has been reported for Si nanocrystals and therefore, the surface states of a-Si QDs appear to enhance the charge-loss rate in the group-B sample. These results suggest that the design and a fabrication of a new functional memory device, which has nonvolatility and multiple charge states achieved by the magnitude of the applied voltage, can be performed by controlling the density of surface states and the a-Si QDs.

In summary, electron charging and discharging was observed in a-Si QDs embedded in silicon nitride films grown by PECVD when the applied voltage was increased in a stepwise manner without changing its sign. This charging effect, which is found only in samples in which most of a-Si QDs were positively charged, can be explained by the transfer of electrons between a-Si QDs. The surface states, due to nitrogen dangling bonds at the surface of the a-Si QDs, were found to be related to the positively charged a-Si QDs and to greatly influence the characteristics of electron storage and long-term charge retention in the a-Si QD MIS structures.

This work was partially supported by the National Research Laboratory Program on Nanophotonic Semiconductors in Korea.