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Charge spectroscopy of Si nanocrystals in a SiO_2 matrix

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For the first time, the recharging of semiconductor nanocrystals (NCs) embedded in a dielectric matrix was studied by means of charge deep-level transient spectroscopy (Q-DLTS). Our measured Q-DLTS spectra were found to arise from two or three transient processes with different activation energies observed in different temperature ranges. We suggest that these are associated with quantum-confined electronic states in Si NCs. The data obtained were used to extract the energy position of NC levels, the size of NCs, and the typical recharging times of weakly coupled NCs.

1 Introduction The reproducibility of recharging characteristics of Si nanocrystallites (NCs) embedded within a thin SiO_2 layer has enabled a better understanding of the charging processes of NCs as well as the development of various devices**.** The aim of the present study was to analyze the recharging process of Si NCs embedded in the thick SiO_2 layer of a metal-oxide-semiconductor structure by the charge deep-level transient spectroscopy (Q-DLTS) technique. Few attempts to apply another variant of DLTS technique (capacitance DLTS, C-DLTS) to study dielectric layers with semiconductor NCs demonstrated only interface traps [1,2]. Our results reveal for the first time that the recharging of Si NC quantum-confined electronic states in the interfacial layer of SiO_2 can be monitored by Q-DLTS measurements.

2 Experimental details Two NC:SiO_2 structures (NC-1 and NC-2) were fabricated by magnetron co-sputtering of Si and quartz sources separated at 96 mm. The Si substrates were n-type Si wafers with a resistivity of 1 Ohm·cm. The time in which the NC:SiO_2 layer was deposited onto the substrate was 30 min for both samples. The thickness of the NC:SiO_2 layer was about 400 nm for both samples. The Si phase content, which varied along the Si substrate, was determined by utilizing the thickness profiles of Si-only and SiO_2-only layers that were sputtered previously. The Si phase (crystalline and/or amorphous) content in the Si-SiO_2 films will be given here by their volume %, x. We found that, over the 100 mm substrate, the Si content varied from 5 to 94%. After deposition, the samples were annealed at 1150°C for 40 min to form NCs in the SiO_2 matrix. The relation of the crystalline / amorphous Si phases for sample NC-1 was higher than that for sample NC-2.

The experimental procedure used in the present study included measurements of capacitance-voltage (C-V) characteristics (at a 1-MHz frequency), current-voltage (I-V) characteristics, and Q-DLTS spectra. A mercury probe or Ag contacts were used for these measurements. An Q-DLTS system employed in the present work enabled us to maintain a fixed sample temperature and to vary scan rate window τ_m during the measurement procedure [3]. Here, $\tau_m = (t_2 - t_1)/\ln(t_2/t_1)$, where t_1 and t_2 are the times at which the Q-DLTS signal $\Delta Q = Q(t_2) - Q(t_1)$ was registered. Q-DLTS measurements were made at different points on the sample with different contents of the Si phase in the NC:SiO_2 layer.

3 Experimental results The Q-DLTS spectra taken on the low-Si-content areas of the samples (x < 15 vol.% for sample NC-1 and x < 30 vol.% for sample NC-2) exhibited no peaks. As we see in Fig. 1 at higher-Si-contents,

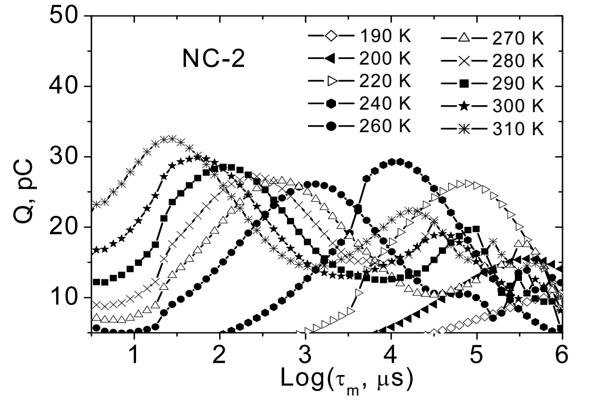

Figure 1 Q-DLTS spectra of the samples NC-2 (67% Si). The constant voltage was 0 V and the filling pulse amplitude was +6 V.

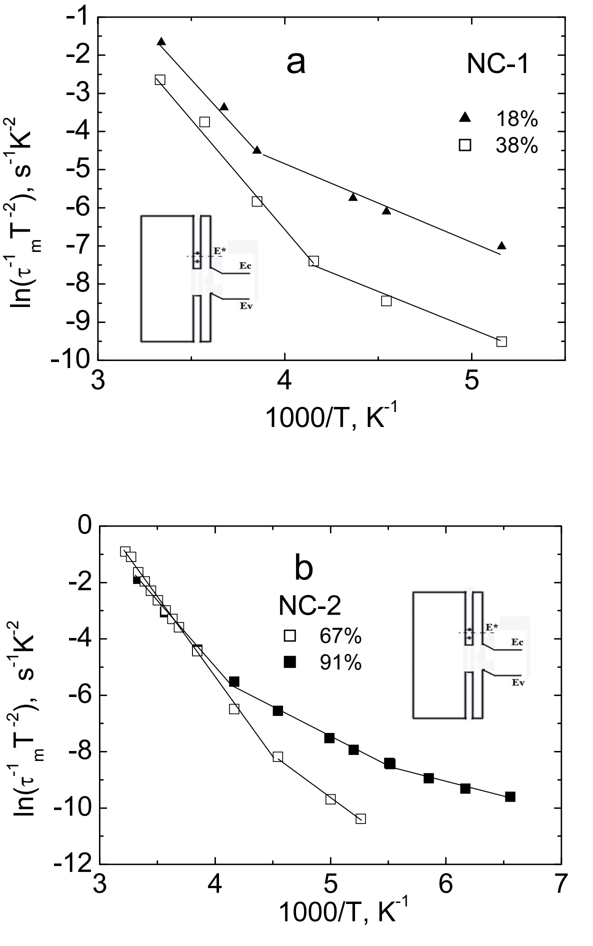

Figure 2 Arrhenius plots of the Q-DLTS peaks as measured at different points along the samples NC-1 and NC-2. The Si contents are indicated in the figure. Inserts demonstrate band diagrams during (a) and after (b) the filling pulse.

one main DLTS peak was found in the Q-DLTS spectra. Following other papers in which quantum-dot parameters were extracted by DLTS [4,5], we assume here that the rate of carrier emission from a trap is e = $\tau_m^{-1} \sim \sigma T^2 \exp(-E_a/kT)$, where σ is the carrier capture cross-section of the trap, k is the Boltzmann constant, and T is the measurement temperature. Each peak was observed in a broad temperature range, making it possible to extract from the Arrhenius plots shown in Fig. 2, two or three activation energies in different temperature ranges. As seen in Fig. 3, the density of charged traps was found to increase with the increasing density of the NCs. The energy levels corresponding to the peaks observed in the Q-DLTS spectra as taken from different points of the samples are summarized in Fig. 4. The cross-section of the traps extracted from the Q-DLTS measurements had anomalously low values that were of the order of 10^{-17} – 10^{-24} cm^2. The transition from the highest activation energy to lower activation energy is accompanied by a decrease in the cross-section by 1-2 orders of magnitude.

4 Discussion The main result of the present study is the observation of Q-DLTS peak which exhibited two or three activation energies in different temperature ranges. It can be hypothesized that the transient processes relating to these energies were connected with the charging of quantum-confined electronic states in Si NCs. This suggestion is supported by the following arguments: (i) There was no peak observed in a low-Si-content part of the sample and in the SiO_2-only reference sample. (ii) The trapped charge density increased with an increase of the Si content. This density was of the same order of magnitude as the density of Si NCs in the vicinity of the SiO_2/Si interface. (iii) The cross sections σ for the observed transient processes were too small to be attributed to deep-level centers in the Si substrate or to interfacial traps. Most probably, the low value of σ is a consequence of the following two factors: a contribution due to tunneling of charge carriers into the NCs and a lower value of the density of states N_c in Si NCs in comparison with the value of N_c in silicon, which was used in the above estimation of σ. (iv) The charging kinetics of the deep states demonstrates that none of the Q-DLTS peaks observed in the spectra could be attributed to deep-level centers in the Si substrate of the examined structures. (v) A lower density of traps observed by the Q-DLTS in the sample NC-2 in comparison with the one found in the sample NC-1 is associated with the lower concentration of Si NCs in the former.

The suggested band diagram of the structure with Si NCs at U > 0 (during the filling pulse) is given by the insets of Fig. 2. During the filling pulse the electrons are captured by Si NCs and after the end of the filling pulse the trapped electrons have to be ejected back from the NCs to the substrate.

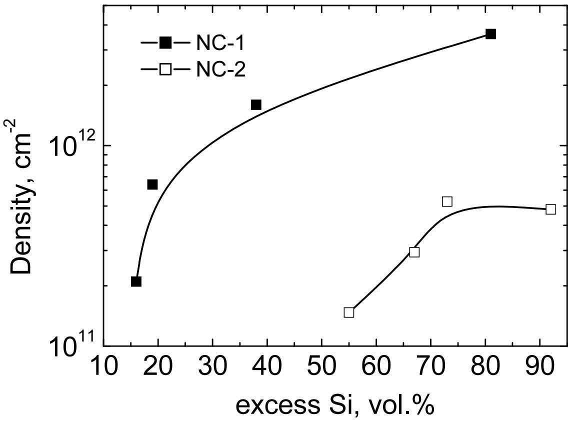

Figure 3 The density of traps that could be charged in the Q-DLTS measurements versus the Si content of samples NC-1 and NC-2.

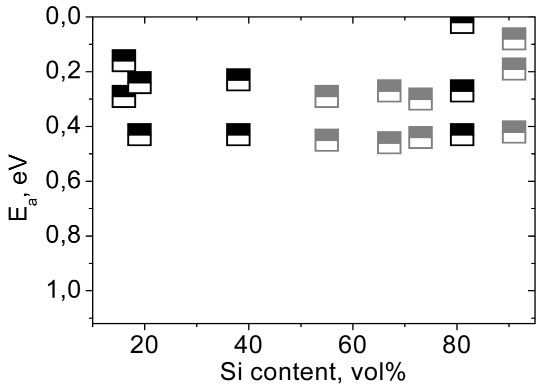

Figure 4 The activation energies extracted from the Q-DLTS spectra versus the Si content. Black and gray points are related to samples NC-1 and NC-2, correspondingly.

The band diagram for U ~ 0 V (this voltage was used in the present Q-DLTS measurements to observe the charge relaxation in the samples) implies depletion of the interfacial region in the silicon substrate (see inset in Fig. 2). We assume therefore that the depopulation of Si NC states in NC:SiO_2 proceeded through electron tunneling via some trap level E* in the barrier. The origin of the level E* suggested to be the traps in the barrier or near the interface.

The activation energies observed experimentally have to be dependent not only on the NC sizes, but also on the band bending induced by interfacial traps. The background trap density in the oxide is slightly varied over the samples. For a comparison of the experimental data with theory for estimation of the NC diameter W we have to consider the energy separation between the levels involved in the tunnel process rather than the absolute values of level energies. The energy levels for the ground and excited electron states in a spherical Si quantum dot embedded in SiO_2 in the effective mass approximation were calculated in [6]. An alternative way to estimate the energy levels in the NCs is by using the well-known formula (see, e.g. [7]) $E_n = \hbar^2/2m(\pi/W)^2n^2$, where E_n is the energy of the n-th confined level and m is the electron effective mass of electrons in Si. These approximations yield Si NC sizes values of 5.6 - 3.3 nm, respectively. All the values of the NC sizes extracted from our Q-DLTS data are realistic and comply with transmission electron microscopy values for the same samples, which fall in the range of 3-5 nm. The typical size of NCs in our samples estimated from the spectral position of the NC-related peak observed in the photoluminescence spectra is 3.6-5.5 nm.

5 Summary Charging of nanocrystallites embedded in a SiO_2 matrix was examined by Q-DLTS in NC:SiO_2/Si structures fabricated by co-sputtering of Si and SiO_2. Q-DLTS peak which demonstrated two or three activation energies displayed in different temperature ranges, were observed. These traps were identified as quantum-confined electronic states in Si NCs. The NC size estimated from the experimentally observed system of deep traps in the system was found to be in good agreement with the microscopy and photoluminescence data taken on the same samples.

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