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C–V and DLTS studies of radiation induced Si–SiO_2 interface defects

I. Capan [a,*], V. Janicki [a], R. Jacimovic [b], B. Pivac [a]

[a] Rudjer Boskovic Institute, 10000 Zagreb, Croatia
[b] Jozef Stefan Institute, 1000 Ljubljana, Slovenia

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ABSTRACT

Interface traps at the Si–SiO_2 interface have been and will be an important performance limit in many (future) semiconductor devices. In this paper, we present a study of fast neutron radiation induced changes in the density of Si–SiO_2 interface-related defects. Interface related defects (P_b centers) are detected before and upon the irradiation. The density of interface-related defects is increasing with the fast neutron fluence.

1. Introduction

Over the past several years one of the most expanding research field in the area of nanoelectronics are three-dimensionally confined semiconductor nanocrystals in the oxide matrix. The reason is their promising application in nonvolatile memories [1] and third generation solar cells [2]. The number of studies dealing with electrical properties is increasing, and among them the capacitance–voltage measurements (C–V) of metal-oxide-semiconductor (MOS) structures containing Si or Ge nanocrystals have attracted a considerable attention. Recently, it has been shown, that semiconductor–oxide interface has a strong influence on charge trapping properties of Ge nanocrystals in SiO_2 matrix [3]. Moreover, it has been proposed to use reactor neutron flux for doping Ge nanocrystals in SiO_2 matrix [4]. While irradiation with thermal neutrons leads to doping of nanocrystals, irradiation with fast neutrons leads to appearance of radiation-induced damage. The interest in neutron transmutation doping (NTD) comes from one of its main advantages over the other methods for doping. It is high-precision doping, because the concentration of impurities introduced at a constant neutron flux is proportional to irradiation time [5]. The question that arises is what is the influence of radiation-induced defects on "as-grown" interface-related defects in such systems? In particular, defects introduced with fast neutrons irradiation. It has been known for many years that MOS structures are extremely sensitive to radiation because electrically charged defects build up in the oxide layer. However, an overview of the literature data showed that most of studies were dealing with X and ^{60}Co gamma rays [6]. The influence of reactor neutrons is still unclear.

In this work, we present a preliminary study of reactor neutrons irradiation induced interface-related defects in Si–SiO_2 structures. We have taken the Si–SiO_2 structures without semiconductor nanocrystals in the oxide. Furthermore, we have eliminated thermal neutrons (as much as possible) with cadmium shields in the reactor, as they will be used only for doping of nanocrystals. This paper addresses two issues: (1) what is the influence of fast neutron irradiation on Si–SiO_2 interface related states, and (2) how can we study those states by the means of DLTS.

2. Experimental details

The single crystal Si(100) substrate used in this study was prepared by Cemat Silicon S.A. (Warsaw, Poland). The substrate was phosphorous-doped with initial resistivity in the range 10–20 Ω cm. SiO_2 film was thermally grown at an oxidation temperature of 1000 °C in a [$H_2 + O_2$] atmosphere (wet oxide). The obtained oxide thickness was 50 nm.

The samples were irradiated with 0.7 MeV neutrons in the carousel facility (CF) of the TRIGA Mark II reactor of the Jozef Stefan Institute in Ljubljana, Slovenia. Neutron irradiations were done inside a cadmium box with thickness of 1 mm to filter out the thermal neutrons. The effective cut-off energy of Cd is 0.55 eV, with distribution maximum for fast neutrons at 0.7 MeV [7]. The flux of fast neutrons was constant at 2.6×10^{10} cm^{-2} s^{-1}, and the accumulated fluences were 1.6×10^{12}, 7.8×10^{12} and 1.6×10^{13} cm^{-2}. The temperature of the samples during irradiation did not exceed 30 °C.

For the gate metallization Au was used. The MOS capacitor area was 0.8 mm^2. High-frequency C–V characterization was performed at different temperatures. All DLTS spectra were taken with a SULA Technologies spectrometer.

* Corresponding author. Tel.: +385 1 456 1111; fax: +385 1 468 0114.
E-mail address: capan@irb.hr (I. Capan).

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3. Results and discussion

Fig. 1 shows high-frequency (1 MHz) C–V measurements at room temperature for all samples. The samples are referred to as S_{asprep} (as prepared), S-IR-1 (irradiated with the fluence of 1.6×10^{12} cm^{-2}), S-IR-2 (irradiated with the fluence of 7.8×10^{12} cm^{-2}) and S-IR-3 (irradiated with the fluence of 1.6×10^{13} cm^{-2}) in the following text (Table 1). This steplike form or "S-shape", observed for all samples, is typical for the MOS structures on n-type Si substrate in the case of high frequency measurements [8]. For the positive voltage the capacitance reaches its maximum value (accumulation region), while for the negative voltage the capacitance is reducing to the minimal value (inversion region). No significant changes have been detected upon irradiation in samples S-IR-1 (Fig. 1b) and S-IR-2 (Fig. 1c), while the most considerable changes (in depletion region) have been observed in the S-IR-3 sample (Fig. 1d), i.e. upon irradiation with the highest fluence. It is known that, for small positive gate voltages, the surface is depleted and the space-charge region charge density dominates. Trapped interface charge capacitance also contributes. The total capacitance in depletion region is the combination of C_{ox}, C_b and C_{it} [9], where C_{ox}, C_b and C_{it} are oxide, substrate and interface capacitances, respectively. The changes in C_b are expected to be minimal, as explained later, so we strongly believe that changes observed in the S-IR-3 sample (Fig. 1d) are mostly interface and/or oxide related. The more detailed separation of those contributions is not possible.

Information regarding the energy distribution and the density of traps are crucial for the future device applications. To obtain those information deep level transient spectroscopy (DLTS) could be used. The DLTS is a well established technique which is commonly used in studying the trap states in the semiconductors [10], and recently it has been applied in studying the semiconductor nanocrystals [11]. However, it is well known that application of DLTS to study interface-related defects is extremely difficult due to the several reasons. The most important are:

(i) The capacitance base line shift; DLTS signal is measured as a function of temperature (usually in a range from liquid nitrogen temperature to room temperature). The scanning of the temperature causes a change in the capacitance signal due to the thermal dependence of the electron emission rate. The important assumption is $\Delta C \ll C$ i.e. the measured traps make only a small contribution to the sample total capacitance. This is not the case for the interface traps.

(ii) Fermi level pinning effect; the shift of the accumulation region to higher voltages (observed for MOS structures) has been explained by the Fermi level pinning effect. The magnitude of the Fermi level pinning depends on temperature. More details regarding those issues are given elsewhere [12,13].

Table 1
The Si–SiO$_2$ samples description with associated fast neutron fluence. Activation energies (ΔE_a) and densities (D_{it}) of interface-related defects estimated from the DLTS.

Sample	Neutron fluence (cm^{-2})	ΔE_a (eV)	D_{it} (eV^{-1} cm^{-2})
S_{asprep}	–	0.27 ± 0.01	1.9×10^{11}
S-IR-1	1.6×10^{12}	0.27 ± 0.02	7.7×10^{10}
S-IR-2	7.8×10^{12}	0.27 ± 0.01	1.3×10^{11}
S-IR-3	1.6×10^{13}	0.23 ± 0.01	1.4×10^{11}

We have performed C–V measurements at low temperatures (250, 200 and 150 K) in order to check the Fermi level pinning effect, but significant shift of the accumulation region to higher voltages has not been observed. It implies that the density of interface related traps is not too high, as the shift of the accumulation region is directly connected to the density of interface traps.

Taking into account all the facts, we have selected temperature interval (100–180 K) and the optimal voltage settings (bias at 0 or −1 V) for DLTS measurements. The voltage settings have been chosen in order to make the capacitance signal coming from the interface to be the most important [9].

Fig. 2 shows DLTS spectra for all samples at the same rate window, τ = 5 ms. Only one trap with temperature maxima at 123, 142, 152 and 145 K for the S_{asprep}, S-IR-1, S-IR-2 and S-IR-3 sample, respectively, has been detected. Irradiation did not introduce new traps in DLTS spectra. Activation energies of electron emission have been determined from Arrhenius plot of $\ln(e_n/T^2)$ versus $1/kT$ as 0.27, 0.27, 0.27 and 0.23 eV for the S_{asprep}, S-IR-1, S-IR-2 and S-

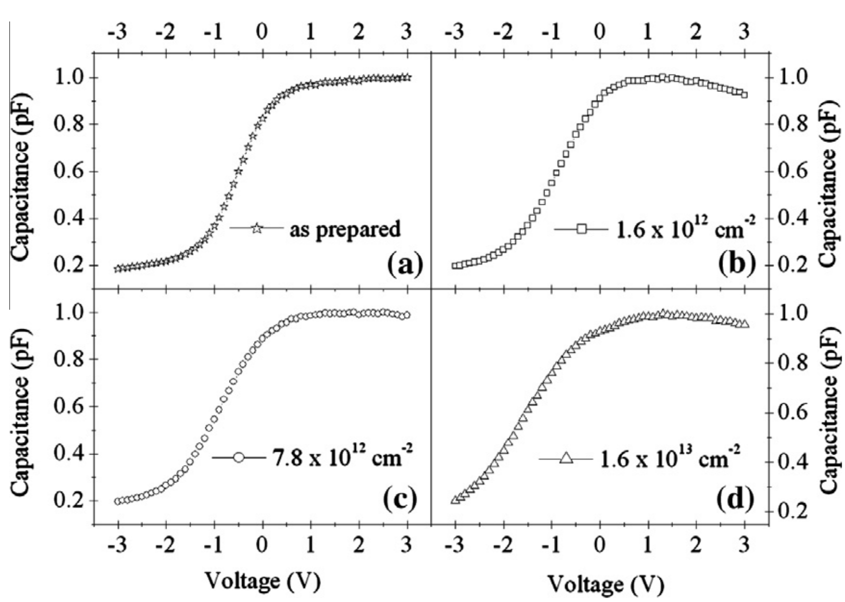

Fig. 1. The normalized (1 MHz) C–V measurements at room temperature for all samples: (a) as prepared MOS structure, (b) irradiated with neutron fluence of 1.6×10^{12}, (c) irradiated with neutron fluence of 7.8×10^{12} and (d) irradiated with neutron fluence of 1.6×10^{13} cm^{-2}.

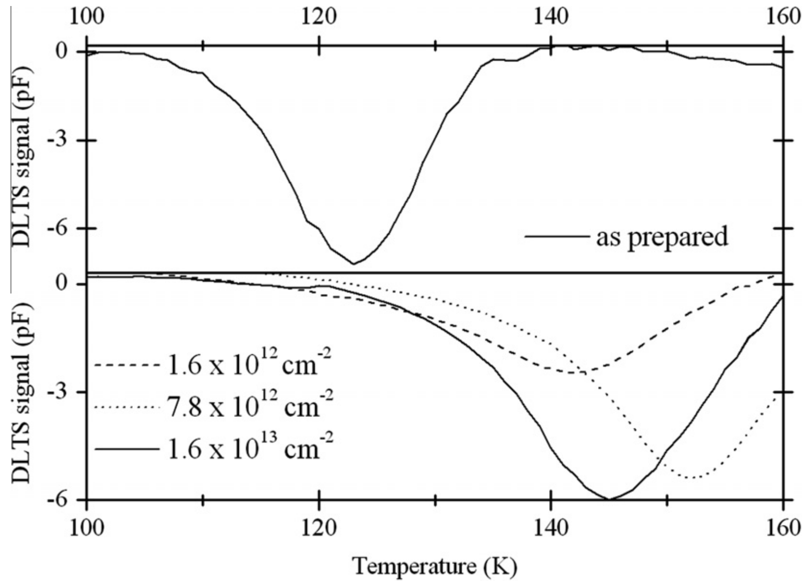

Fig. 2. DLTS spectra for all samples (as prepared MOS structure and irradiated with different neutron fluences of 1.6×10^{12}, 7.8×10^{12} and 1.6×10^{13} cm^{-2}). Rate window, τ = 5 ms.

IR-3 sample, respectively (Table 1). Although the temperature maximum is not the same for all traps, the estimated activation energies are identical, except the trap observed in the S-IR-3 sample.

The obtained value of 0.27 eV (S_{asprep}, S-IR-1 and S-IR-2) is slightly shifted toward lower energies comparing to the value of 0.3 eV, which is quoted in a large number of papers where DLTS measurements on the P_b centers are reported [12–14]. The shift of 0.03 eV is almost within the error, see Table 1. We have ascribed our 0.27 eV trap to the P_b centers-related trap, which exist in the upper half of the silicon band gap. The origin of 0.23 eV trap is not yet so clear. Due to the broadening of DLTS peak it is possible that some shift in the activation energy will occur. Moreover, this sample was irradiated with the highest fluence so it is highly expected that we have introduced much more damage, oxide damage in particular. It is known that radiation response of $Si–SiO_2$ structures involves several different processes. The most important, among them, are [6]:

(i) Generation of electron–hole pairs.
(ii) Hopping transport of holes through localized states to the interface.
(iii) Deep hole trapping near $Si–SiO_2$ interface.
(iv) Radiation-induced interface traps.

Moreover the *C–V* measurements for this sample (Fig. 1d) have shown the most significant changes (in depletion region). It is reasonable to assume that this defect is more complex, and has a several contributions. One of the components is interface-related. Another component is most likely due to the changes in the oxide. The reasons we have neglected changes in the bulk are following:

(i) The most common radiation induced traps in silicon have not been detected by DLTS.
(ii) The neutron fluence used in this study is not expected to introduce many electrically active defects in Si substrate with initial resistivity of 0.02–0.2 Ω cm.

Further studies are needed in order to completely understand the origin of 0.23 eV.

The interface state densities D_{it} have been estimated for all traps according to [15]:

$$D_{it} = \frac{\varepsilon_r \varepsilon_0 A N_D C_{ox}}{C_q^3 kT} \Delta C \tag{1}$$

where C_q is the quiescent capacitance, ΔC is the amplitude, A the capacitor area, N_D the semiconductor doping concentration, C_{ox} the capacitance in accumulation, and T the temperature of the peak maxima. The estimated values are given in Table 1. The obtained values are low, for the S-IR-1 sample in particular. However, this result fits very well the fact that we have not observed the Fermi level pinning effect. Moreover, the obtained values show interesting behavior. Upon the low fluence irradiation the density of interface-related traps is lowered, compared to the as grown sample. As the neutron fluence is increasing the density of interface related traps is increasing, i.e. is "reaching" the initial value. Similar behavior has been reported by Benedetto et al. [16]. Contrary to our study, they have used ^{60}Co and X-ray for irradiation. In their work, they have shown that the interface states density will increase with the dose of irradiation. However, they have shown that the growth rate of the interface states depends on the initial density of the interface states. In the case of samples with the largest D_{it} (the value is the same as in our study, 2×10^{11} eV^{-1} cm^{-2}), the slowest rate of growth ($D^{1/2}$) has been reported [16]. The result we have obtained is different, as for the lowest dose of irradiation the density of interface states has reduced, compared to the initial (pre-irradiation) value.

We have used thermally grown wet oxide in our study so the hydrogen influence should not be neglected. The interaction of hydrogen (H^+ and/or H^0) with radiation induced defects (holes, predominantly) in the formation and passivation of interface states (P_b states) is still an open question. Similar to our findings Awazu et al. [17] have shown that small doses of gamma irradiation reduce the density of interface states.

Therefore, initial decrease in the density of interface states can be attributed to the radiolitic formation of atomic hydrogen in the close vicinity of the interface which passivated the defects. Upon further irradiation the defect rate production increased and the diffusion limited hydrogen passivation at room temperature is not so effective any more.

4. Conclusions

We presented a study of fast neutron irradiation induced changes at $Si–SiO_2$ interface by means of *C–V* and DLTS. We have shown that prior the irradiation, P_b centers-related trap is present. Upon initial decrease, the density of interface-related traps is increasing with the fast neutron fluence.

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