Journal of ELECTRONIC MATERIALS, Vol. 49, No. 9, 2020
https://doi.org/10.1007/s11664-020-08080-3

TOPICAL COLLECTION: 18TH CONFERENCE ON DEFECTS (DRIP XVIII)

Charging Effects in Al-SiO$_2$-*p*-Si Structures After Low-Energy Electron Beam Irradiation

P.S. VERGELES,[1,2] YU.O. KULANCHIKOV,[1] and E.B. YAKIMOV[1]

1.—Institute of Microelectronics Technology and High Purity Materials RAS, Chernogolovka, Russia. 2.—e-mail: vergelesp@gmail.com

The effect of electron beam irradiation on trap charging and interface defect generation in Al/SiO$_2$/Si structures was investigated by high-frequency capacitance–voltage measurements. Irradiation was carried out with two beam energies, at which the electron penetration depth was smaller and larger than the SiO$_2$ thickness. The effect of applied bias, which changes the electric field inside the SiO$_2$ film and the Si surface potential, on both the interface defect generation under the electron beam irradiation and their annealing was revealed. This showed that excess electrons generated by an e-beam play an important role in the interface defect formation. It was found that interface trap relaxation can occur even at room temperature, likely by electron tunneling from Si or hole tunneling from SiO$_2$. The relaxation of positive bulk charge occurs at temperatures higher than 400 K via thermally stimulated carrier escape from traps. The activation energy for this process was estimated as 0.35–0.4 eV.

Key words: SiO$_2$, electron beam irradiation, interface charge, C–V characteristics

INTRODUCTION

Insulators and dielectric materials are very important in modern semiconductor technology. It is well known that such materials can be electrically charged under different types of ionizing irradiation (x-ray and gamma radiation, proton and electron beams, alpha particles, etc.), and thus the study of charging dynamics and its relaxation is of great interest for many fields of science and technology, including radiation hardness of semiconductor devices, development of insulating materials for the protection of satellites and spacecraft, electron beam lithography, and electron and ion spectroscopy analytical techniques.[1,2] Previous studies can be roughly divided into two groups: investigations of surface potential due to irradiation,[3,4] and studies of fixed oxide charge and traps at the dielectric/semiconductor interface formed in thin dielectric films by irradiation with x-ray or low-energy electron beams.[1,2] Surface potential due to charging can reach a few kiloelectronvolts,[3] which can deflect an electron beam and decrease its apparent energy under electron beam lithography or electron microscopy characterization. Ionizing radiation generates electron–hole pairs inside the dielectrics, and these excess carriers can diffuse and/or drift in the self-consistent field. As a result, positive and negative charge distributions are formed due to different electron and hole diffusivity and mobility. As shown in Ref. 4, the resultant surface potential formation cannot be explained without taking into account these spatial distributions. The difference between electron and hole distribution produces the net charge distribution, which leads to the appearance of internal electric fields and affects the charging dynamics even for dielectrics with thickness exceeding the ionization particle penetration depth. It is well known that in the case of SiO$_2$ film on Si, irradiation creates

(Received November 19, 2019; accepted March 13, 2020;

interface states at the SiO$_2$/Si interface and generates a positive charge inside SiO$_2$.[1,2] This leads to the formation of a self-consistent electric field, which can significantly affect the underlying device properties. The resulting electron and hole distribution depends on their mobility, self-consistent electric field and concentrations, energy levels, and capture cross-sections of traps. However, less is known about these parameters due to the complexity of the physical processes involved, which prevents the development of a comprehensive theoretical picture. Information concerning electron and hole transport can be obtained by generation of excess carriers close to the upper surface and by applying additional bias under irradiation. However, to the best of the authors' knowledge, such measurements have not been carried out up to now. In the overwhelming majority of previous studies on the effects of irradiation in SiO$_2$/Si structures, the size of the excess carrier generation region exceeds the film thickness.

In the present paper, the effect of irradiation by electrons with a penetration depth less than the SiO$_2$ thickness is studied. The external bias is applied under both irradiation and room temperature relaxation. This enables a better understanding of electron and hole contributions in the interface state formation.

EXPERIMENTAL

Metal–oxide–semiconductor (MOS) capacitors consisting of 200-nm-thick thermally grown SiO$_2$ film on p-Si doped with boron at a concentration of 3×10^{14} cm^{-3} were used in the investigations. Lower ohmic contact was produced by rubbing the eutectic Al-Ga alloy in the backside of the Si substrate. Twenty-nanometer-thick Al layers with a diameter of 1.5 or 2 mm were thermally evaporated on the SiO$_2$ film and used as the upper metal contacts. Capacitance–voltage (C–V) high-frequency measurements were carried out at room temperature using a C–V plotter PAR Model 410 operating at 1 MHz. Irradiation of the structures under study was carried out through the metal contact in the scanning electron microscope (SEM; JEOL JSM-840A) in TV mode at electron beam energies E_b equal to 2.5 and 10 keV, and maximum beam current I_b of about 1 nA. At E_b = 2.5 keV, the primary electrons do not reach the SiO$_2$/Si interface (electron range $R \sim 100$ nm), while at E_b = 10 keV, $R \sim 1000$ nm, and the primary electrons reach the interface and penetrate into Si. Normalized distribution of the rate of generation for both energies calculated by the Monte Carlo method are shown in Fig. 1. It should be pointed out that while the electron–hole generation rate for 10 keV electrons is weakly dependent on a depth increasing to the Si/SiO$_2$ interface, the rate for 2.5 keV electrons has a sharp maximum at about 30 nm. Therefore, most of the experiments were carried out with this energy, as it enables the role of hole and electron transport in the observed effects to be analyzed separately. Taking into account that the total deposited energy for 10 keV electrons is four times that for 2.5 keV electrons, it can be shown that the total energy deposited inside the SiO$_2$ film, and thus the number of electron–hole pairs per primary electron, is approximately the same for both energies used. In most cases, an irradiation dose of 20 μC/cm^2 was used for E_b = 2.5 keV to obtain a measurable effect. The irradiation dose for E_b = 10 keV was varied from 6.25×10^{-2} to 1 μC/cm^2. Under irradiation, the investigated structures were grounded or a bias of both positive and negative polarities was applied between lower and upper contacts. Annealing of irradiated structures was carried out in a temperature range of 295 K to 483 K.

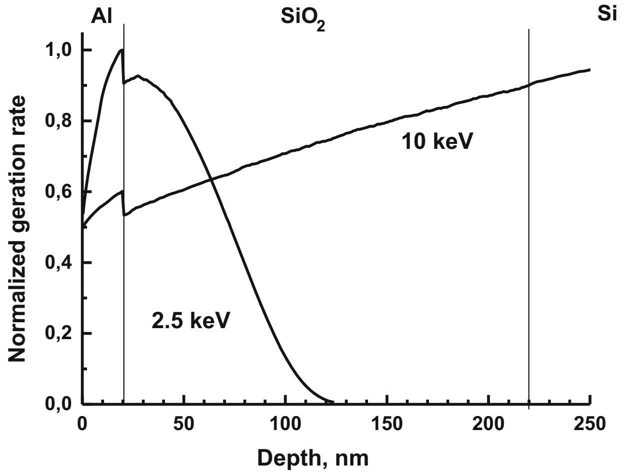

Fig. 1. Depth–dose distributions for E_b equal to 2.5 keV and 10 keV, calculated for the structure studied. Interface positions are shown with thin vertical lines.

RESULTS AND DISCUSSION

C–V curves measured before and after irradiation with beam energy E_b equal to 2.5 keV and 10 keV are shown in Fig. 2a and b, respectively. The corresponding apparent charge densities calculated from a difference between the experimental and theoretical curves as a function of surface potential in Si are shown in Fig. 2c and d. It should be noted that even before irradiation, a shift in the C–V curve of about −10 V relative to the theoretical curve can be observed. As seen in Fig. 2c and d, this shift is determined by the positive charge present inside the SiO$_2$ layer, which is evaluated from the flat-zone voltage shift ΔV_{FB}. This charge is rather stable and does not change even by applying bias of ± 40 V. Some interface energy states are also revealed.

After low-energy electron beam irradiation (LEEBI) with 2.5 keV energy and a dose of 20 μC/cm^2, a noticeable change in C–V curves can be seen. The transition from accumulation to inversion becomes shallower, although the shift in the inversion region is rather small (Fig. 2a, c). It is widely

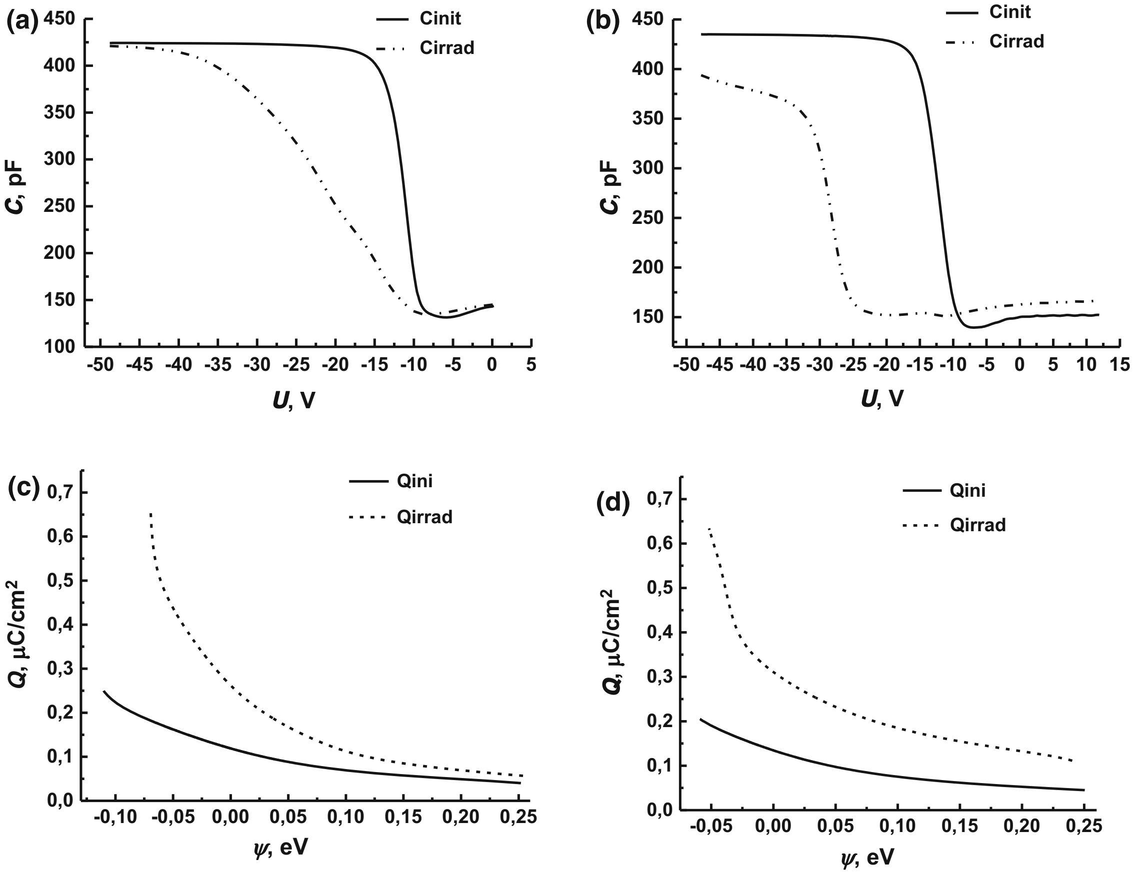

Fig. 2. C–V curves measured before and after irradiation by an electron beam (a) with E_b of 2.5 keV and an irradiation dose of 20 μC/cm^2, and (b) with E_b of 10 keV and an irradiation dose of 1 μC/cm^2. The corresponding charge densities as a function of surface potential ψ in Si for irradiation with (c) 2.5 keV and (d) 10 keV electrons.

accepted[5] that a charge trapped inside SiO_2 can be estimated from a shift in flat-band voltage ΔV_{FB}; however, as seen in Fig. 2, after LEEBI with 2.5 keV energy, there is almost no shift in the C–V curve in the inversion relative to that before irradiation. Thus, it seems reasonable to assume that in structures irradiated with 2.5 keV electrons, a voltage shift determined by the "bulk" charge is rather small, and the main changes consist in the trap formation at the Si/SiO_2 interface. These traps can capture holes from Si (or inject electrons into Si) under the C–V measurements.

At energy of 10 keV, the electron penetration depth is larger than the SiO_2 thickness; therefore, the excess carriers generated can charge SiO_2 throughout its depth. Thus, irradiation with 10 keV electrons produces much larger ΔV_{FB}, which allows us to assume that the bulk positive charge in SiO_2 in this case is larger than that after 2.5 keV irradiation. This seems to contradict the fact that a near-surface SiO_2 layer at E_b = 2.5 keV should be positively charged (the electron emission coefficient is larger than 1) and at E_b = 10 keV should be negatively charged due to the electron emission coefficient dependence on E_b.[3] However, it should be taken into account that the secondary electrons are emitted from a very thin near-surface layer, and the resulting charge in our experiments is screened by the metal contact. ΔV_{FB} in MIS structures is proportional to $\int_0^{t_{ox}} x\rho(x)\mathrm{d}x$,[5] where x is the distance from the metal contact, and $\rho(x)$ is the net charge density; therefore, it is more sensitive to the charge near the Si/SiO_2 interface than to that near the metal contact. For this reason, ΔV_{FB} is determined not only by the value of irradiation-induced charge, but also by its depth distribution inside the SiO_2 layer. As seen in Fig. 1, for E_b = 10 keV, electron–hole (e–h) pairs are generated over the entire SiO_2 thickness, while for E_b = 2.5 keV, the maximum rate of electron–hole generation occurs at a depth of 30 nm. It should also be taken into account that an electric field formed by a positive charge in the unirradiated structure prevents the hole transport to the Si/SiO_2 interface, and the metal contact screens a near-surface positive charge formed by 2.5 keV irradiation. This may explain the small apparent "bulk" positive charge created by 2.5 keV e-beam irradiation, as seen in Fig. 2c. The results obtained in Ref. 6 showed that the traveling distance of a hole generated by an e-beam is less than a few tens of nanometers. One theory predicted a mean hole drift length of a few nanometers.[7] Thus, it is reasonable to assume that at least for electron irradiation with E_b = 2.5 keV, the interface states are built up by electrons. This contradicts the widely accepted scenario,[1,2] according to which the excess electrons are quickly swept out of the oxide, typically in picoseconds or less, although a portion of them could recombine with excess holes. The holes that escape recombination are captured inside the SiO$_2$ film, causing a negative V_{FB} shift. Other holes can move in the electric field to the Si/SiO$_2$ interface, and when they reach it, they can build up interface traps at the interface. Thus, the widely accepted scenario assumed that only holes are responsible for the interface state buildup. However, the results obtained show that electrons generated by the e-beam are also involved in this process.

As the electric field can significantly affect the electron and hole drift inside SiO$_2$, it was interesting to study charging effects under a bias applied during irradiation. The C–V curves measured after irradiation with E_b = 2.5 keV electrons and positive or negative applied bias are shown in Fig. 3. Irradiation with a negative bias up to −30 V and beam energy of 2.5 keV results in almost no change in the density of interface states in comparison with zero bias irradiation, but leads to a slight increase in the V_{FB} shift to negative voltages. If a positive bias is applied, the V_{FB} shift to the negative voltages increases significantly with the bias, and its slope also becomes shallower; thus both the apparent bulk positive charge and the interface state density increase. Qualitatively similar behavior was observed for irradiation with 10 keV electrons.

Thus, it can be concluded that the dependence of interface defect density on a negative bias applied during irradiation is small and increases slightly at a positive bias. If the interface traps are formed by electrons, it can be explained by taking into account that the electric field stimulating the electron drift to the SiO$_2$/Si interface already exists in the initial structure. It is possible that the additional electric field causes no noticeable change in the number of electrons reaching the interface. At a positive bias, the electrons can be injected from Si, e.g. by the mechanisms responsible for the MIS device degradation.[8,9]

The ΔV_{FB} dependence on applied bias is well resolved at both beam energies used. The negative bias applied to the metal contact under irradiation has almost no effect on charging, while an application of positive bias leads to an essential increase in ΔV_{FB}. At zero bias in the unirradiated structure, the electric field, due to preexisting positive charge, stimulates the electron drift inside SiO$_2$ to the SiO$_2$/Si interface and, as seen in Fig. 2, the Si surface is driven into inversion, which can also stimulate electron tunneling from Si to interface traps. An application of negative bias to the metal electrode repels electrons to the interface even stronger. On the other hand, it moves the Si surface into accumulation that should suppress electron injection from Si and possibly enhance their escape into Si. These mechanisms can compensate each other, and may be a reason for the small increase in positive charge at negative applied bias. The significant increase in ΔV_{FB} at a positive bias is most likely determined by a shift in positive charge distribution from the metal contact due to the hole drift towards the interface and the electron drift towards the metal contact.

To study the stability of e-beam irradiation effects, the relaxation of C–V curves under thermal annealing was investigated. The C–V curves measured after 10 min of isochronous annealing of a structure irradiated with 10 keV electrons are shown in Fig. 4a, and the corresponding charge density dependence on the surface potential in Si is shown in Fig. 4b. It is seen that annealing at temperatures of about 400 K almost completely removed the shallow acceptor interface states, while annealing the states with the weaker dependence on the surface potential (probably the "bulk" states) requires a higher annealing temperature.

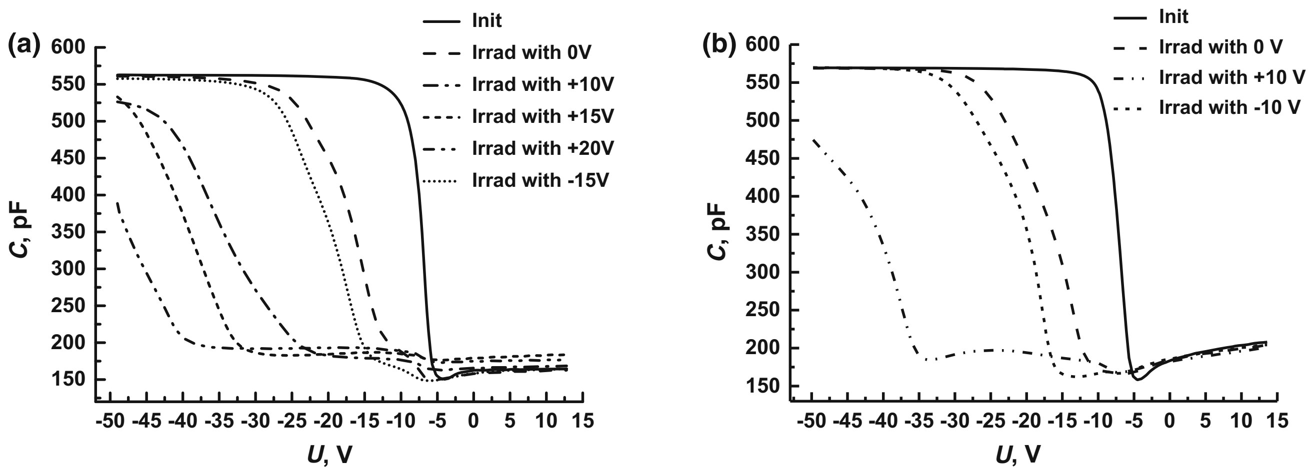

Fig. 3. Irradiation MIS-structure with applied bias: (a) E_b = 2.5 keV, irradiation dose 20 μC/cm^2; (b) E_b = 10 keV, dose—6.25 × 10^{-2} μC/cm^2.

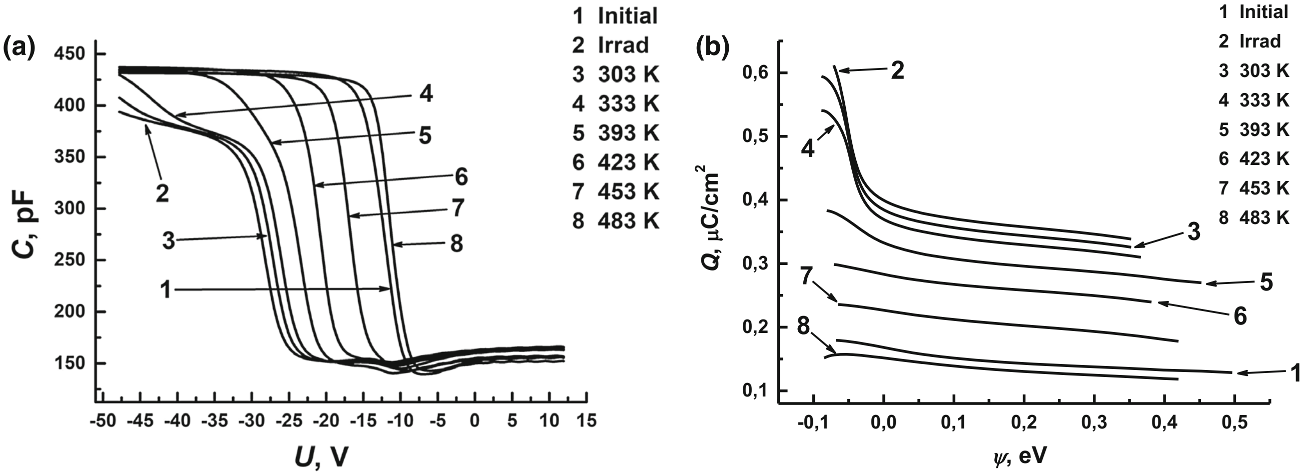

Fig. 4. (a) C–V characteristics after isochronal thermal annealing at different temperatures; (b) the corresponding charge density dependence on the surface potential ψ in Si.

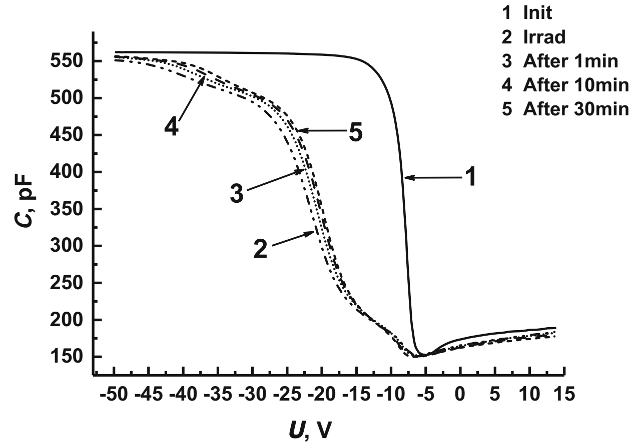

Fig. 5. Restoration of C–V curves under storage at room temperature. Irradiation energy 2.5 keV, irradiation dose 30 μC/cm^2.

Annealing at 483 K practically returned the C–V curves to those before irradiation, which correlates well with the results obtained in Refs. 10,11.

As seen in Fig. 5, the interface states start to disappear even at room temperature. The relaxation of voltage shift (and therefore the density of interface traps) in a temperature range from room temperature to 393 K can be described as $\Delta V = \Delta V_0 - A \times \ln(t/t_0)$, where ΔV_0 is the voltage shift after irradiation, t is the annealing time, and A and t_0 are some constants. The relaxation follows this law up to about 400 K. Such dependence is shown in Fig. 6a (curve 1) and b for room temperature and 393 K, respectively. Usually such logarithmic dependence was explained by the charge relaxation determined by tunneling of holes from interface defects into Si or electrons from Si to the interface defects[10,12] with a further transformation of preexisting interface defects. If so, a bias applied under relaxation should affect this process. As shown in Fig. 6a (curve 2 and 3), this is indeed the case, i.e. a positive bias applied to the metal contact enhances the relaxation and a negative bias suppresses it. Thus, the observed dependence on applied bias does not contradict the tunneling mechanism. It should be noted that at room temperature, this process is rather slow; thus an extrapolation of relaxation rate shows that 50% of introduced interface traps disappear in 2.5–3 months. In reality, this time can be even greater, because the electric field, and therefore the tunneling probability, will decrease with a decrease in interface charge.

At temperatures higher than 400 K, the bulk charge effectively begins to relax, and it seems that at such temperatures the relaxation mainly occurs via a carrier escape from the traps. Estimation of the activation energy for the carrier escape gives a value of 0.35–0.4 eV, which correlates well with the value of 0.35 eV obtained in Ref. 13 for electron traps in thermally grown SiO_2. Nevertheless, it should be noted that the relaxation of bulk charge includes not only carrier escape, but also their drift and possible re-trapping. The voltage shift, as mentioned above, is proportional to $\int_0^{t_{ox}} x\rho(x)\mathrm{d}x$. Therefore, the dependence of charge annealing dynamics on time and temperature can be rather complex and could modify the obtained activation energy value. Another point which should be mentioned is the incomplete irradiation annealing effects. Indeed, as noted above, an application of bias of ± 40 V at room temperature has practically no effect on the C–V curve of the initial sample. However, after annealing, despite the restoration of C–V curves, an application of such bias at room temperature leads to a small but noticeable shift. Such a "memory effect" determines the dependence of irradiation and annealing effects on treatment history and will be studied in greater detail in the future.

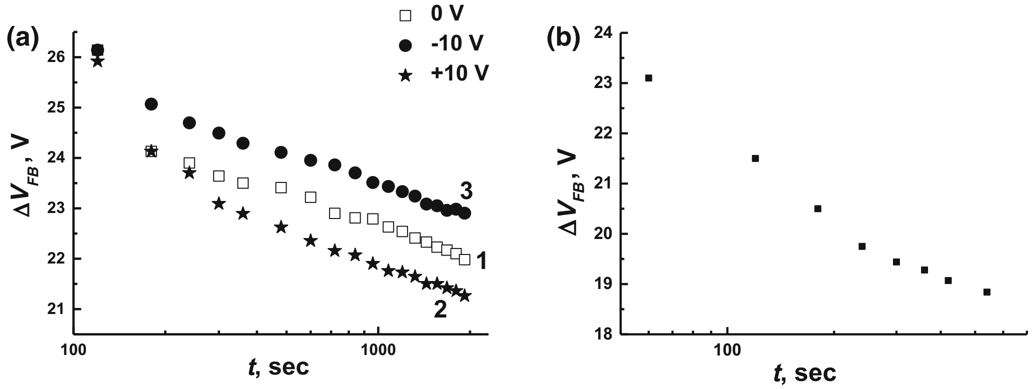

Fig. 6. ΔV_{FB} dependence versus time annealing: (a) at room temperature for zero and ± 10 V applied bias; (b) at 393 K annealing temperature. Irradiation energy 2.5 keV, irradiation dose 20 μC/cm^2.

CONCLUSION

In this work, the effect of electron beam irradiation on trap charging and interface defect generation in Al/SiO_2/Si structures was studied by high-frequency capacitance–voltage measurements. The use of low-energy e-beam treatment and application of bias under irradiation allowed us to obtain information about electron and hole transport in SiO_2. In particular it was shown that, contrary to what is assumed in the literature, not only are holes involved in interface state generation, but electrons contribute as well. The relaxation of trapped charge and interface states and its dependence on temperature and applied bias were studied. At temperatures lower than 400 K, the relaxation of irradiation effects occurred mainly due to interface state annealing, while at higher temperatures, carrier escape from the bulk traps mainly contributed to the relaxation.

ACKNOWLEDGMENTS

The work of P.S. Vergeles and Yu.O. Kulanchikov was supported in part by the State Task No. 007-00220-18-00 and of E.B. Yakimov by the RFBR Grant No. 18-02-00035.

REFERENCES

1. T.R. Oldham, *IEEE Trans. Nucl. Sci.* 50, 483 (2003).
2. J.R. Schwank, *IEEE Trans. Nucl. Sci.* 55, 1833 (2008).
3. E.I. Rau, S. Fakhfakh, M.V. Andrianov, E.N. Evstafeva, O. Jbara, S. Rondot, and D. Mouze, *Nucl. Instrum. Methods Phys. Res. B* 266, 719 (2008).
4. E.I. Rau, E.N. Evstaf'eva, and M.V. Andrianov, *Phys. Solid State* 50, 621 (2008).
5. D.K. Schroder, *Semiconductor Materials and Device Characterization*, 3rd ed. (Hoboken: Wiley, 2006), pp. 319–369.
6. S.S. Borisov, P.S. Vergeles, and E.B. Yakimov, *J. Surf. Invest. X-ray Synchrotron Neutron Tech.* 4, 754 (2010).
7. I.A. Glavatskikh, V.S. Kortov, and H.-J. Fitting, *J. Appl. Phys.* 89, 440 (2001).
8. D. Vuillaume, A. Bravaix, and D. Goguenheim, *Microelectron. Reliab.* 38, 7 (1998).
9. M. Cho, P. Roussel, B. Kaczer, R. Degraeve, J. Franco, M. Aoulaiche, T. Chiarella, T. Kauerauf, N. Horiguchi, and G. Groeseneken, *IEEE Trans. Electron Dev.* 60, 4002 (2013).
10. A.J. Lelis, T.R. Oldham, H.E. Boesch Jr, and F.B. McLean, *IEEE Trans. Nucl. Sci.* 36, 1808 (1989).
11. J. Zhang, I. Pintilie, E. Fretwurst, R. Klanner, H. Perrey, and J. Schwandt, *J. Synchrotron Radiat.* 19, 340 (2012).
12. M. Schmidt and H. Köster Jr, *Phys. Status Solidi (b)* 174, 53 (1992).
13. P.A. Dement'ev, E.V. Ivanova, and M.V. Zamoryanskaya, *Phys. Solid State* 61, 1394 (2019).