Semiconductor Physics, Quantum Electronics & Optoelectronics, 2011. V. 14, N 3. P. 334-338.

PACS 07.57.-c, 61.43.Dq, 61.72.Dd, 68.35.Dv, 78.60.Hk, 78.66.-w

Effect of magnetic field on the reconstruction of the defect-impurity state and cathodoluminescence in Si/SiO_2 structure

L.P. Steblenko[1], O.V. Koplak[2], I.I. Syvorotka[3], V.S. Kravchenko[1]
[1]Taras Shevchenko Kyiv National University, Department of Physics,
64, Volodymyrs'ka str., 01601 Kyiv, Ukraine,
[2]Research and Training Center "Physical and Chemical Materials Science"
under Taras Shevchenko Kyiv National University and NAS of Ukraine
64, Volodimirska str., 01033 Kyiv, Ukraine, e-mail: o.koplak@gmail.com
[3]Scientific Research Company "CARAT", 202, Stryis'ka str., 79031 Lviv, Ukraine

Abstract. Impurity states in Si/SiO_2 structure have been studied using cathodoluminescence (CL). It has been found that intrinsic structure defects in Si/SiO_2 are sensitive to the action of magnetic field, which can be revealed due to changes in Si/SiO_2 optical properties. The most sensitive to magnetic field (about 35 per cent) is the intensity of the 1.9 eV CL band attributed to non-bridge oxygen atoms.

Keywords: silicon, defects, magnetic field, cathodoluminescence.

Manuscript received 30.12.10; accepted for publication 14.09.11; published online 21.09.11.

1. Introduction

The Si/SiO_2 system is a basis of modern microelectronics. The growth of thermal oxide on the silicon surface is accompanied by occurrence of a number of diverse physico-chemical processes, nature of which has not been elucidated yet. Nevertheless, the physical properties of the formed phase boundary, which determine the parameters of planar devices, are reflection of the oxide film structure [1]. One of the most informative methods for diagnostics of structural defects and impurities in thermal oxide films on silicon is the cathodoluminescence (CL) [2]. As indicated in [2], CL using a focused beam of high-energy electrons for luminescence excitation has a number of advantages over photoluminescence. First of all, high energy of electrons (1 keV and higher) provides excitation of all luminescence centers present in the oxide. Secondly, there is a possibility to obtain spectra from different depths of the film, since the penetration depth is a function of electron energy [3]. At the energy of 1 keV electrons penetrate SiO_2 into a depth of 200 Å.

The CL spectra of thermal oxide films on silicon are determined by the type of substrate and the film formation conditions [2, 4]. Nowadays, for efficient application of Si/SiO_2 systems in optoelectronics, used are various techniques of silicon dioxide modification. The authors of [4] have found a high-power-electron-beam-induced modification of silicon dioxide, which consists in appearance of additional CL bands attributed to structural defects, specifically, to Si clusters. In this case, the source for formation of Si clusters is SiO_2 irradiated by electrons. According to [4], Si clusters appear as a result of irradiation and local heating-up of silicon dioxide by electron beam, which cause changes in the cathodoluminescent properties of microvolume. The authors of [5] have found that CL bands in the green spectral region (2.0–2.5 eV) are observed when the energy transferred to a unit volume (e.g., under action of electron beam) exceeds certain threshold. In [5] it is shown that irradiation by electrons creates interstices, which are present in silicate systems, free Si nanoclusters. The authors of [5] suppose that appearance of green luminescence in this case can be related to Si/SiO_2 phase boundary. In literature, there is also evidence for the effect of electric field on the charge state of ion-implanted Si/SiO_2 structures [6]. The work [7] reports a change in the intensity of the 2.8 eV CL band in nanocomposit glass after treatment of initial samples in electric field. Taking into account the importance of the problem related to the structure of silicon dioxide, in our opinion, it is worthwhile searching for and developing the other methods of its modification.

In recent years, the researchers' attention has been attracted by the possibility of modification of the

structure and the structure-dependent, e.g., optical properties of non-magnetic materials and structures based on them by using weak ($B \le 1$ T) magnetic fields [8-11]. In this relation, the aim of this work was to study the changes in the cathodoluminescent properties of amorphous silicon dioxide grown on silicon under action of weak constant magnetic field.

2. Experimental

Experimental samples were Si/SiO_2 structures obtained by thermal oxidation of p-Si(111) boron-doped single-crystal silicon wafers in dry oxygen atmosphere at 1050 °C. The thickness of SiO_2 oxide layer was measured ellipsometrically and comprised 250 nm. As-grown samples were then stored under room conditions for a year. Cathodoluminescence of Si/SiO_2 structures was studied in a vacuum cryostat ($P = 10^{-4}$ Pa) at liquid nitrogen temperature. The experimental setup is shown in Fig. 1.

Cathodoluminescence of the samples was excited by electron gun pulses. The parameters of electron beam were as follows: electron energy 10 keV, beam current 100 μA, pulse duration 2 μs, repetition rate 30 Hz. The electron beam was focused on the sample surface into a round spot 1 mm in diameter. The luminescence spectra were recorded using the diffraction grating monochromator DMR-4 and detected by a photomultiplier tube of FEU – 106 type within the spectral region 1.0 to 5.0 eV. Magnetic treatment (MT) was carried out by exposing the Si/SiO_2 structures to a weak constant magnetic field with an induction $B = 0.17$ T for $t_{1MT} = 7$ days and $t_{2MT} = 15$ days. Studied in this work was a relative effect of magnetic field on the CL spectra. The CL spectra of Si/SiO_2 structures were measured in the identical conditions (energy of electrons in the beam, current value, pulse duration, etc.) at the same temperature.

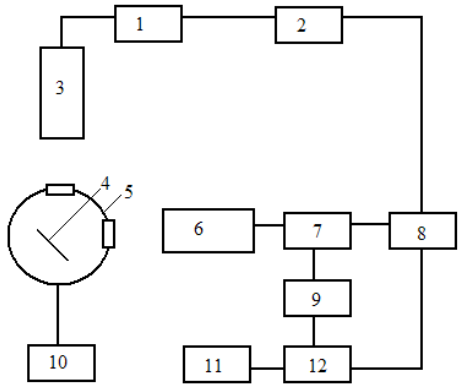

Fig. 1. Experimental setup for studying cathodoluminescence of Si/SiO_2 structure: 1 – electron gun power supply; 2 – pulsed generator; 3 – electron gun; 4 – Si/SiO_2 sample; 5 – cryostat; 6 – monochromator; 7 – photomultiplier tube; 8 – PM tube power supply; 9 – preamplifier; 10 – roughing-down pump; 11 – recording device; 12 – lock-in amplifier.

3. Results and discussion

The results of CL study in Si/SiO_2 structures are presented in Fig. 2 a – c . The CL spectra of the samples after MT for both MT durations used are similar in their shape to the spectra of the reference samples, they are well reproducible and consist of 6 bands, too. The CL bands of Si/SiO_2 structure after action of magnetic field showed, in general, the same peak positions as for the reference samples and were well described by Gaussian shapes, although their intensities were different (Fig. 2c).

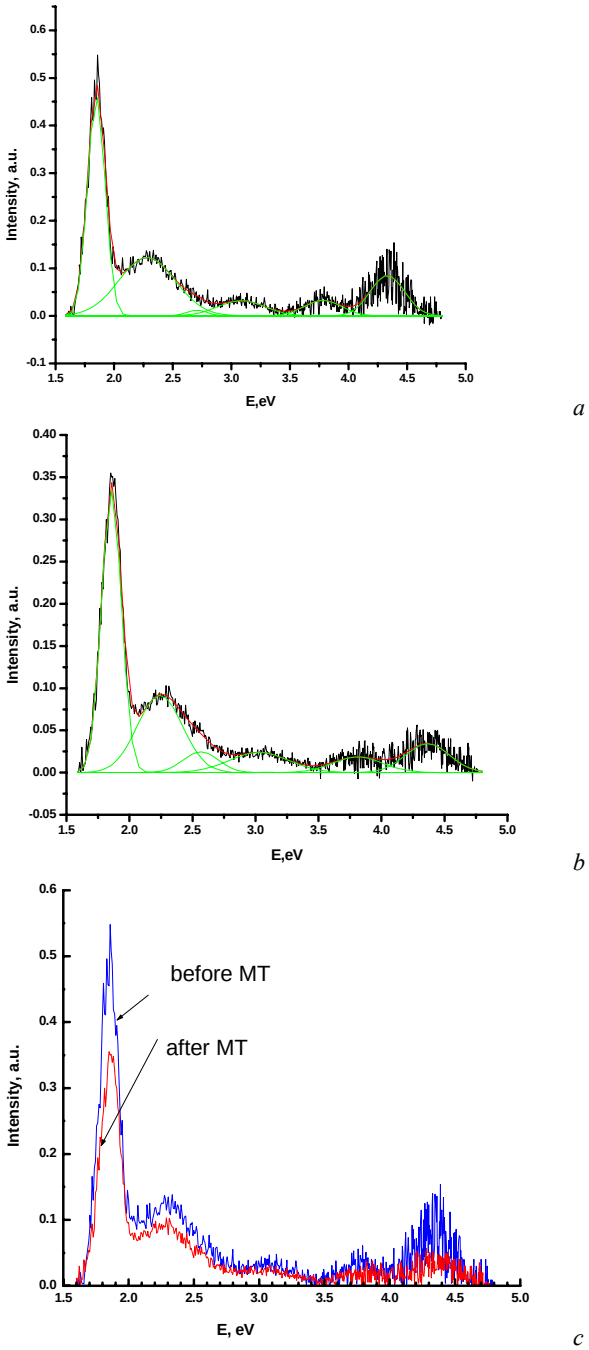

Fig. 2. Cathodoluminescence spectra of Cz-*p*-Si/SiO_2 structure: *a* – before magnetic treatment (MT), *b* – after MT ($B = 0.17$ T for $t_{MT} = 15$ days), *c* –CL spectra before and after MT.

Identification of the bands in the CL spectra was carried out by comparing them with the respective bands taken from literature. In this work, we have identified the intrinsic-defect-related bands with the peaks at 1.90 ± 0.05, 2.65 ± 0.10 and 4.40 ± 0.07 eV in the reference samples. These bands were well approximated by Gaussian shapes with the half-widths of 0.14 ± 0.02, 0.17 ± 0.01 and 0.29 ± 0.01 eV, respectively (Fig. 2a).

It is suggested in [2, 6, 12] that the red emission band at 1.9 eV may be related to excitation of non-bridge oxygen atom. Non-bridge oxygen produces a luminescence band with the peak at 1.9 eV which corresponds to absorption bands at 2.0 and 4.75 eV.

So, red emission with the peak at 1.9 eV excited within absorption bands at 2.0 and 4.75 eV is attributed to the centers related to defects of silicon-oxygen tetrahedron (i. e., non-bridge oxygen). As noted in [12], the emission band that corresponds to a 4.75-eV absorption band may be caused by the presence of hydroxyl impurity. The centers of red luminescence are non-bridge oxygen atoms (O_1^0), i. e., oxygen radicals

$$\left(-\mathrm{Si}-\mathrm{O}_0\right), \left(\mathrm{O}_3 \equiv \mathrm{Si}-\mathrm{O}\right)$$

which are formed on the breakage of oxygen-hydrogen bonds in hydroxyl groups. The neutral center of a free radical of non-bridge oxygen atom (O_1^0) is an elementary intrinsic defect in glassy silica. In the crystalline state (the long range ordering), this kind of defects cannot be stabilized [12]. Therefore, the luminescence band peaked at 1.9 eV and excited at 4.75 eV is identified as that related to non-bridge oxygen.

According to [4, 5], the appearance of intense emission in the green region with a peak at 2.2–2.3 eV is due to the presence of silicon nanoclusters in SiO_2. It should be noted that there are alternative interpretations of the origin of the green 2.3 eV band in the CL spectra of thermal films. Thus, in [13] this band is related to the existence of Si/SiO_2 interface, while in [12] this band is attributed to exciton emission. In the latter case, under high-energy excitation the autolocalised exciton emission is observed at 2.6 eV for quartz, at 2.3 eV for amorphous SiO_2, and at 2.2 eV for cristobalite [14].

The blue band at 2.65 eV, which was observed in the CL spectra, is due to forbidden singlet-triplet transitions in the molecular complex of twofold-coordinated silicon atom [4]. Most likely, this defect is a silicon atom that has only two neighbouring oxygen atoms [4].

The 4.4-eV band that we observed in the CL spectra, according to the authors of [15], is also related to twofold-coordinated silicon (O_2 = Si:), a defect known as a silylene center. Silylene centers are believed to be formed as a result of displacement of atoms from the sites of SiO_2 lattice [15] in the process of ion implantation or in the processes of growth and theatments [16]. Also, there are alternative opinions on the mechanism inherent to formation of twofold-coordinated silicon. Thus, the authors of [17] suggest that ion implantation results in formation of that kind of defects due to breakage of two $\mathrm{Si}-\mathrm{O}$ bonds in the same $\mathrm{Si}-\mathrm{O}$ tetrahedron during the implantation process.

In the UV region, we have observed the band at 3.1-3.2 eV that is attributed to a small content of boron impurity in the Si/SiO_2 interface [4]. Appearance of this band is caused by the presence of boron dopant in the single-crystal silicon used as substrate.

As our experiments have shown, a weak magnetic field influences the CL spectra (Fig. 2 b – c). Comparison of the CL spectra presented in Fig. 2c shows that magnetic treatment decreases the intensity of all the CL bands considerably (from 23 up to 35 per cent). Especially strong are the changes in the intensities of the CL bands at 1.9 eV (attributed to non-bridge oxygen) and 4.4 eV (twofold-coordinated silicon). In our opinion, the decrease in the CL intensity may be caused by the reconstruction in the centers of radiative recombination, which are intrinsic structural defects in Si/SiO_2. Our previous studies [18, 19] have shown that magnetic treatment of single-crystal silicon wafers with a natural silicon dioxide film results in changes in the structure of both silicon and oxide film, which, in turn, alters the defect-impurity state of the near-surface layer of the crystal. From the literature [8, 10, 11], it is known that action of a weak magnetic field on non-magnetic materials initiates the processes of chemical bond breakage in structural defect nanoclusters, stimulates processes of diffusional instability and adsorption, increases the rate of interdefect solid state reactions.

A possible mechanism of magnetic field effect on the evolution of metastable complexes that are present in Si/SiO_2 structure and have been detected in our study is rearrangement of valence electrons in the atoms of point-defect complexes ($\mathrm{Si}-\mathrm{OH}$, $\mathrm{Si}-\mathrm{H}$, $\mathrm{Si}-\mathrm{O}-\mathrm{Si}$, $\mathrm{Si}-\mathrm{O_x}$ precipitates, etc.) due to spin-dependent processes. The force and energy U_M, imposed by magnetic field with an induction of $B \sim 1$ T on a structural element in magnetically disordered medium is negligible and at room temperature (T_R = 300 K) comprises $U_M \approx g\mu_B B << kT_R$, where g is the Lande factor, μ_B is the Bohr magneton, and k is the Boltzmann constant. In such a situation, the magnetic field cannot affect the equilibrium state of the thermodynamic system. Consequently, a weak magnetic field can influence effectively only non-equilibrium systems (spin systems), which pass in their evolution through short-lived excited states, in which multiplicity can be changed. A constant magnetic field is able to alter the multiplicity of non-equilibrium spin-correlated pairs of paramagnetic defects only if the energy difference between their singlet and triplet states $E_S - E_T$ is of the same order of magnitude as the energy U_M, that is, when the covalent bond is weakened. Being in such a magnetosensitive

state, point defect complexes are expected to show a weaker covalent bond, for which the energy difference between singlet and triplet states is of the same order as U_M and such a "weak" magnetic field can cause S–T transitions. A result of spin conversion is weakening and breakage of chemical bonds in point defect complexes.

These and other processes that are initiated by the action of magnetic field are followed by the processes of structural relaxation, which, in turn, result in structural modification. In this relation, it is reasonable to suppose that non-bridge oxygen (1.9 eV band), twofold-coordinated silicon (2.3 and 4.4 eV), boron impurity (3.1 eV band) and other defects that are present in silicon dioxide film, due to action of magnetic field undergo interdefect reactions with, e.g., vacancies and form complexes of oxygen-vacancy ($O-V$) type, which are referred to as type A defects, and complexes type $B-V$ (type E defects), $Si-B$ complexes, etc. It is binding of isolated defects, responsible for the red, green, blue, UV and other CL bands, into abovementioned point defect complexes that leads to decreasing the concentration of the radiative recombination centers and, correspondingly, to quenching the cathodoluminescence. It is worth mentioning that similar results related to a decrease in the photoluminescence intensity in ZnS crystals under action of pulsed magnetic field (B = 7 T) were obtained by authors of [9].

It is not improbable that a magnetic-treatment-induced decrease in the number of twofold-coordinated silicon atoms, the emission centers responsible for the 2.3 and 4.4 eV bands, may occur due to closure of non-saturated (broken in the magnetic treatment) bonds between silicon and neighbouring under-coordinated silicon and oxygen atoms or due to closure of broken bonds of silicon by diffusing hydrogen atoms, which are formed in the oxide layer due to magnetic-treatment-induced dissociation of silylene ($Si-OH$) and hydroxyle (OH) groups.

And now let us say a few words about changes in the green 2.3 eV emission band. As already noted above, this band in the CL spectra may be due to emission of autolocalized excitons in amorphous SiO_2. The magnetic-treatment-induced decrease in the intensity of the 2.3 eV band may be explained as follows. Action of magnetic field leads not only to breakage of chemical bonds in nanoclusters, but also to a decrease in the exciton binding energy, which results in exciton decay. The latter leads to a rise in the number of free carriers and to corresponding drop in the CL intensity. This statement agrees with the results obtained by the authors of [20] in studying the action of magnetic field with an induction of 6 T on the kinetics of photoluminescence of quantum dots in InAs/AlAs. Switching the magnetic field on resulted in a faster decay kinetics [20]. The results obtained are explained in the framework of a model that takes into account a fine structure of exciton levels and their exchange and Zeeman splitting in magnetic field.

So, it may be concluded that the magnetic-treatment-induced changes in the emission spectra revealed in our study may be due to both magnetic-field-stimulated interdefect reactions (and, as a result, appearance of 'new' structural nanoclusters in silicon dioxide itself) and processes in the electron subsystem. A more detailed interpretation of the mechanism of changing the intensities of Si/SiO_2 structure cathodoluminescence bands caused by action of magnetic field requires further investigations, since this fact depends on both a change in defect concentration and a change in the efficiency of luminescence channels.

References

1. V.S. Sokolov, N.A. Fedorovich, Mechanical stresses on the $Si-SiO_2$ interface // *Phys. Status Solidi* (*a*), **99**, No. 1, p. 151-158 (1987).
2. M.V. Zamoryanskaya, V.I. Sokolov, Investigation of the structure of thermal oxide films on silicon by means of cathodoluminescence // *Fizika Tverdogo Tela,* **40**, No. 11, p. 1984-1989 (1998), in Russian.
3. F. Maurice, L. Meny, R. Tixier, Microanalysis and scanning electron microscopy // *Les Editions de Physique*, **2**, p. 527 (1978).
4. L.A. Bakaleynikov, M.V. Zamoryanskaya, E.V. Kolesnikov et al., Modification of silicon dioxide by electron beam // *Fizika Tverdogo Tela,* **46**, No. 6, p. 989-994 (2004), in Russian.
5. V.N. Bogomolov, S.A. Gurevich, M.V. Zamoryanskaya et al., Formation of silicon nanoclusters in silicon substrate modification by electron beam // *Fizika Tverdogo Tela,* **43**, No. 6, p. 357-359 (2001), in Russian.
6. A.P. Baraban, L.V. Miloglyadova, V.I. Ter-Nersesyants, Effect of electric field on the charge state of ion-implanted silicon-silicon dioxide structures // *Pis'ma Zhurnal Ekspiment. Teor. Fiziki,* **27**, No. 3, p. 89-94 (2001), in Russian.
7. V.V. Afrosimov, B. Ber, V.V. Zhurikhina et al., Mass transfer in thermal electric-field-induced modification of glassy metallic nanocomposites // *Zhurnal Tekhnich Fiziki*, **80**, No. 11, p. 53-61 (2010), in Russian.
8. Yu.I. Golovin, R.B. Morgunov, Magnetoplastic effects in crystals // *Izvestiya RAN. Ser. Fiz.*, **61**, No. 5, p. 850-859 (1997), in Russian.
9. Yu.I. Golovin, R.B. Morgunov, A.A. Baskakov et al., Effect of magnetic field on plasticity, photo- and electroluminescence of ZnS single crystals // *Pis'ma Zhurnal Ekspiment. Teor. Fiziki,* **69**, No. 2, p. 114-118 (1999), in Russian.
10. R.B. Morgunov, Spin micromechanics in plasticity physics // *Uspekhi Fiz. Nauk*, **174**, No. 2, p. 131-153 (2004), in Russian.

11. M.N. Levin, B.A. Zon, Effect of pulsed magnetic fields on Cz-Si crystals // *Zhurnal Ekspiment. Teor. Fiziki,* **111**, No. 4, p. 1373-1397 (1997), in Russian.
12. A.R. Silin, A.N. Trukhin, *Point Defects and Elementary Excitations in Crystalline and Glassy SiO_2.* Riga, Zinatne Publishers, 1985 (in Russian).
13. V.N. Bogomolov, Capillary phenomena in extremely thin zeolite channels and metal-dielectric interaction // *Phys. Rev. B,* **51**, No. 23, p. 17040-17045 (1995).
14. A.N. Trukhin, A.E. Plaudis, A study of intrinsic luminescence of SiO_2 // *Fizika Tverdogo Tela,* **21**, No. 4, p. 1109-1113 (1979), in Russian.
15. A.P. Baraban, D.V. Egorov, Yu.V. Petrov et al., Electroluminescence of SiO_2 layers with excessive silicon // *Pis'ma Zhurnal Tekhnich Fiziki*, **30**, No. 2, p. 1-5 (2004), in Russian.
16. V.S. Vavilov, V.F. Kiselev, B.N. Mukashev, *Defects in Silicon and on its Surface*. Moscow, Nauka Publishers, 1990 (in Russian).
17. A.P. Baraban, L.V. Miloglyadova, Defects and defect formation in oxide layer of ion-implanted structures of silicon – silicon dioxide // *Zhurnal Tekhnich. Fiziki*, **72**, No. 5, p. 56-60 (2002).
18. V.A. Makara, M.A. Vasilyev, L.P. Steblenko et al., Magnetic-field-induced changes in the impurity state and microhardness of silicon crystals // *Fizika Tekhnika Poluprovodnikov,* **42**, No. 9, p. 1061-1064 (2008), in Russian.
19. V.A. Makara, M.A. Vasilyev, L.P. Steblenko et al., Effect of magnetic treatment on microhardness and structure of silicon crystal near-surface layers // *Fizika Khim. Tverdogo Tela,* **10**, No. 1, p. 193-199 (2009), in Russian.
20. T.S. Shamirzaev, A.M. Gilinskii, A.K. Bakarov et al., Long-term kinetics of photoluminescence of quantum dots in InAs/AlAs in magnetic field // *Fizika Tekhnika Poluprovodnikov,* (Russia), **39**, No. 1, p. 35-37 (2005).