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Low Energy Electron Emission from Surface-Interface States of SiO_2:Ge Films

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Abstract. In this paper we present the results of optically stimulated electron emission (OSEE) investigation of thin SiO_2 films implanted with Ge^+ ions. The emission models of Urbach rule and power Kane-dependence are used to fit OSEE spectra at different excitation energy ranges. The materials under study may find a number of technological applications in optical devices and ultraviolet sensors. Samples attestation was performed by electron microscopy and x-ray photoelectron spectroscopy (XPS). XPS data revealed strong dependence between the Si, Ge and O atoms state and annealing time. Observed correlations between parameter values of Urbach- and Kane-related models suggest the implantation-induced changeover of both the vibronic subsystem and energy band structure.

INTRODUCTION

High quality silica-based materials are required for the state of the art Si electronic technologies, especially those related to thin oxidized layers used in modern microelectronic devices and optical communications. Ion-beam irradiation of SiO_2 is a convenient tool to create such materials: it provides a direct source for nanocluster formation, though also induces various types of structural defects. Particularly the germanium implantation is used in communication and sensing technology, such as photoinduced Bragg gratings in optical fibers. Wide application prospects of SiO_2 thin films and nanostructured materials cause the necessity of studying their energy structure and electronic properties. However, well-known optical spectroscopy techniques are complicated or not suitable for opaque samples and film-wafer structures. Besides, surface electronic states become crucial in this case, determining the characteristics of the most important technological systems, such as Si-SiO_2 [1]. Knowledge of the SiO_2 surface is rather limited in comparison to the intensively studied surfaces of single crystal metals, semiconductors and crystalline oxides.

Optically stimulated electron emission (OSEE) has been shown to be a useful method in the study of surface and interface properties in thin film insulators, revealing emission "tail" originating from SiO_2 surface electronic states [2, 3]. There is some ambiguity in the interpretation of internal OSEE experiments because of the possible contributions, described by electron emission variants of Urbach [2] and Kane [4, 5] dependences. Approximation by both expressions may yield important parameters of the samples under study.

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In our previous work [2] the electron emission version of well-known optical Urbach rule for low-sized silica modifications was proposed. The present study contains both the Kane- and Urbach-related analysis of OSEE spectral dependencies for thin SiO_2 implanted with germanium ions.

EXPERIMENTAL

The OSEE spectra were recorded in the excitation wavelength range 200–600 nm. The UV radiation was provided by a DDS-400 deuterium lamp using a MSD-2 monochromator. OSEE measurements were carried out in vacuum at a pressure of 10^{-4} Pa with a VEU-6 secondary electron multiplier. The experimental setup made it possible to measure the OSEE spectral response in the temperature interval of 290–500 K. The OSEE spectra obtained in our experiments were normalized against the source light flux.

The samples under study were SiO_2 films (30 nm) dry-oxidized on a p-type silicon substrate, then implanted with Ge^+ ions (E = 20 keV, F = $1\cdot10^{16}$ ions/cm^2) and annealed in Ar protecting environment at 950°C during 15, 30 and 60 seconds. The final atomic concentration profile were calculated by the computer simulation tool TRIDYN including sputtering and swelling processes as well as interface mixing [6]. This program is based on the sputtering version of the TRIM program for multicomponent targets and takes into account compositional changes both due to the spatial distribution of target atoms deposited in collision cascades, and due to the presence of the implanted ions. The local density of the target is allowed to relax according to a given function of the densities of the individual components. The depth dependences of concentrations for both native and embedded atoms after ion implantation are shown on Fig. 1. Maximum atomic percentage of Ge ions reaches 8 % at 18 nm depth. One may notice considerable ion mixing in the ~10 nm area near the Si-SiO_2 interface, causing the oxygen atoms to move forward into silicon, while the Si atoms are scattered back to oxide area.

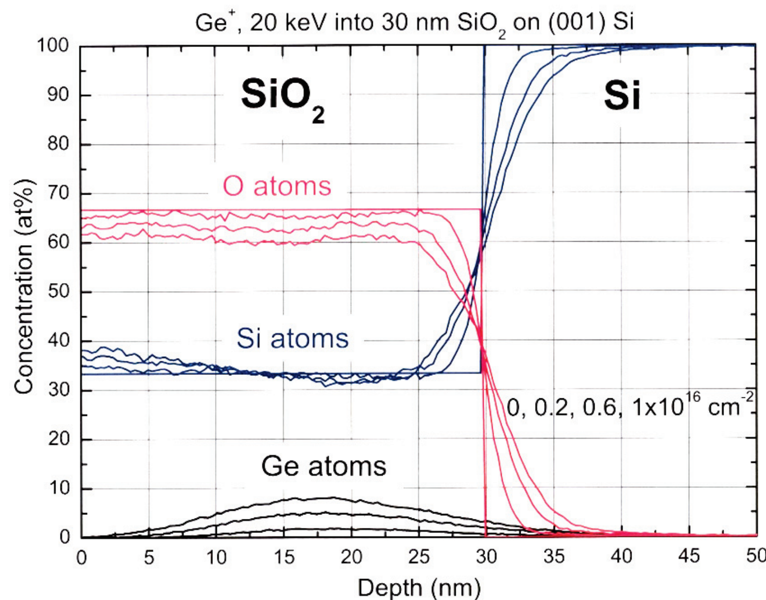

FIGURE 1. Depth distribution of Si, O and Ge atoms after germanium ions implantation into 30 nm SiO_2 film on silicon wafer. Straight lines: virgin, curves: as implanted.

X-ray photoelectron spectroscopy (XPS) of Ge, Si and O core levels was used to characterize the structure-energy state of SiO_2 matrix. The XPS spectra were calibrated using a reference energy of 285.0 eV for the carbon 1s core level. Silicon core levels (Fig. 2) demonstrate chemical shift depending on annealing time, revealing significant perturbations of electronic states of SiO_2 matrix. The maximum shift corresponds to 15 – 30 s annealing time. The XPS method allows registering the electrons coming only from topmost 9 nm layer. In order to characterize the whole volume of SiO_2 matrix we use the OSEE spectroscopy.

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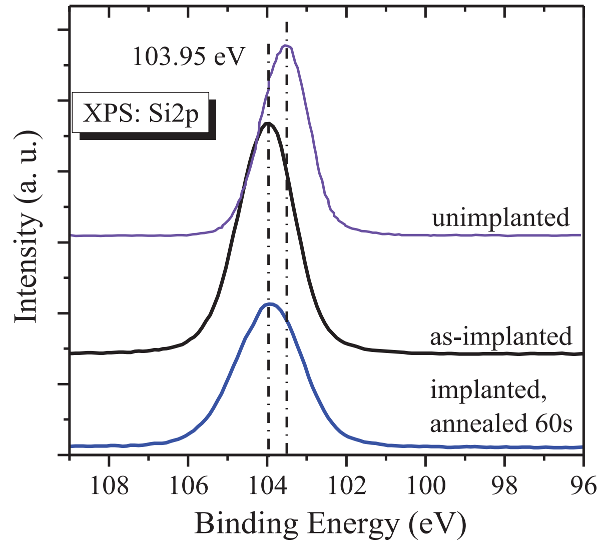

FIGURE 2. Si 2p – core-levels X-ray Photoelectron Spectra: initial sample, implanted samples with 0 s and 60 s annealing times.

SURFACE BAND TAILS REGION (4.4 – 5.2 eV)

The average emission energy of registered OSEE electrons was about 0.3 – 0.8 eV. Urbach rule analysis was applied to the low-energy region of excitation photon spectra (4.75-5.15 eV, see Fig. 3), according to eq. (1) [2]:

$$I(h\nu,T) = I_0 \cdot \exp\left(-\frac{W}{kT}\right) \cdot \alpha(h\nu,T) \ , \tag{1}$$

$$\alpha \sim \exp\left(\frac{h\nu - E_g(T,X)}{E_U(T,X)}\right). \tag{2}$$

Here α(hν, T) is the surface states optical absorption coefficient; W(T) – the surface energy barrier (external work function) for electron exit into vacuum; $E_g(T,X)$ – temperature- (T) and disorder- (X) dependent energy gap width [7]; E_U – Urbach energy.

According to OSEE studies of crystalline and glassy materials [8], the optical absorption stage determines the spectral shape of the OSEE curves. The optical absorption coefficient at the fundamental absorption edge may be described by well-known “crystal-like” or “glass-like” Urbach rule, depending on the type of structural disorder [7]. The authors of [9] proposed a modified rule combining two noted variants.

The spectral curves are described well by OSEE dependences (1) in the 4.5 – 5.2 eV range (Fig. 3). The model parameters as given by approximation are presented in Table 1. The energy gap for silica films (5.5 – 5.8 eV) is lower than the corresponding bulk value of ~ 9 eV that suggests the surface nature of the electron emission centers. In the framework of the OSEE method one cannot distinguish between the contributions of interface and surface states. Therefore, the effective band gap width derived from Urbach approximation takes into account both types of electronic states.

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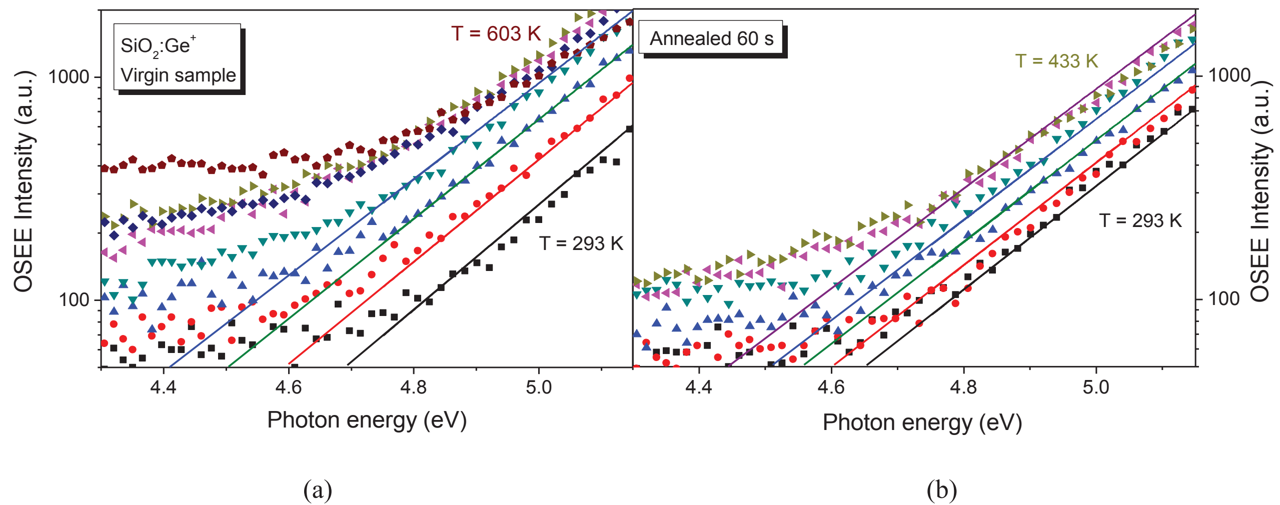

FIGURE 3. OSEE spectra of SiO_2:Ge^+ films, virgin and annealed for 60 s after implantation. The emission variant of Urbach rule is applied (straight lines).

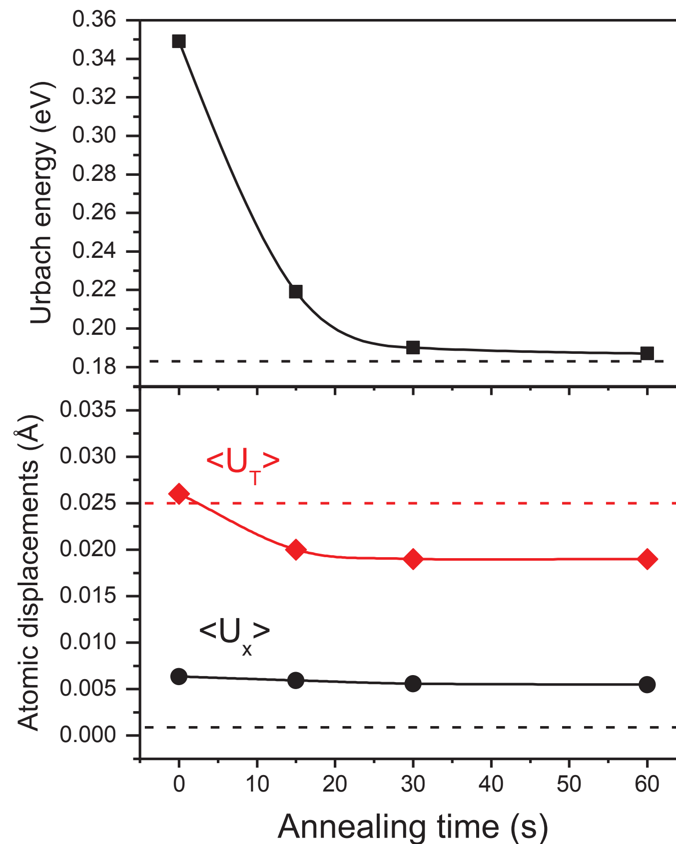

FIGURE 4. Urbach energy (top) and mean atomic displacements due to dynamic <U_T> and static <U_X> atomic disorder (bottom) in their dependence on sample annealing time. All data obtained at room temperatures.

The effective activation parameter W reflects peculiarities of electron transport and exit to vacuum processes. The undisturbed matrix has the biggest energy barrier of 163 meV. Ion implantation reduces its height down to 46 meV, while subsequent annealing restores the W parameter. The effective phonon energies of initial films have values close

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to the deformation-related TO bulk phonon mode of vitreous SiO_2 [10], while ion implantation and annealing lead to higher phonon energies up to 115 meV, revealing the significant matrix reconstruction.

It is seen from Fig. 4 that the parameter of static disorder for SiO_2:Ge is significantly higher than that of films not exposed to ion implantation. Overall disorder level described by E_U value increases after implantation, leading to predominance of the "glass-like" Urbach rule. Numerical analysis according to eq. (1) and "frozen phonons" model [9] allowed to decompose Urbach energy values into two components, corresponding to static and dynamic disorder. As it is seen from the bottom window of Fig. 4, the static atomic displacements increase after implantation and undergo relaxation during annealing. At the same time phonon-related dynamic displacements remain almost the same after ion bombardment, but decrease during the annealing process. The latter change may be related to vibronic subsystem reconstruction indicated by increasing surface phonon energy (Table 1).

ELECTRON EMISSION POWER DEPENDENCES (5.2 – 6.2 eV)

The high-energy excitation of OSEE spectra (5.4-6.2 eV, see Fig. 4) is described by the Kane power law:

$$I = A\cdot(h\nu-\phi)^n, \tag{3}$$

Where A is a magnitude approximation parameter, ϕ – the photoelectric workfunction, n – the power factor, which is related to the dominating type of interband electron transitions and may be equal to 0.5, 1, 1.5, 2 or 2.5, [5]. During the approximation of the experimental data (Fig. 5, a), the power factor n = 2 was chosen in order to maximize the linear part of spectra, which appears in corresponding coordinates. It means that electron emission is mainly due to indirect transitions between surface energy bands. According to the theory of electron emission [5], the threshold energy ϕ should be higher than Fermi energy in this case.

The same factor n = 2 correspond to the indirect interband transitions forming the fundamental absorption band [11]. Thus, we can see again that the optical absorption stage plays a determining role in OSEE processes. One may suggest that the lower energy part of OSEE spectra, described by Urbach rule, also corresponds to indirect electron transitions. From the Table 1 we can see the energy of phonons participating in these transitions. For the implanted film possesses it is nearly the TO phonon mode of SiO_2 lattice.

The Fig. 5, b presents the values of the ϕ parameter for different samples, showing an absolute maximum after 15 s post-implantation annealing. The dashed line represents the ϕ value (5.25 eV) of a virgin SiO_2 film. Work function φ correlates with Si core levels chemical shift, determined by XPS. Its changes should reflect the evolution of surface band gap width, as the electron transport and exit barriers have opposite dependence on annealing time. Parameter *A* also demonstrates sensitivity to silica matrix structure changes.

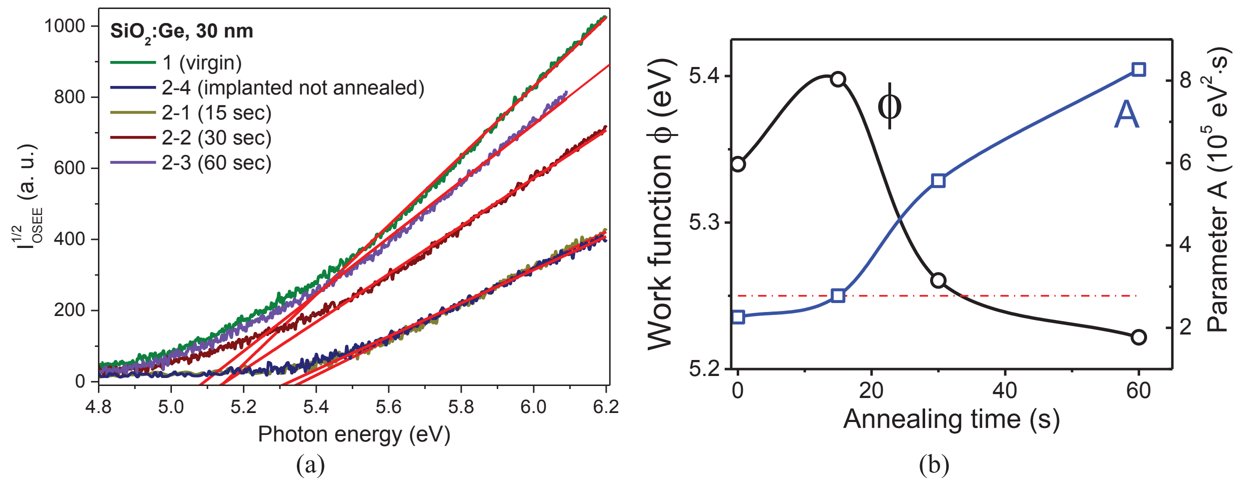

FIGURE 5. (a) OSEE spectra of $SiO_2:Ge^+$ films. Eq. (2) is applied by the straight lines. (b) The plot of parameters ϕ and A against sample post-implantation annealing time. All data obtained at room temperatures.

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Tail parameters	Virgin	Implanted	Annealed 60 s
Activation parameter, W (meV)	163	46	98
Surface phonon energy, ħω (meV)	61.8	93.9	113
Dynamic disorder parameter, $<U_T>$ (Å)	0.025	0.026	0.019
Static disorder parameter, $<U_X>$ (Å)	$9\cdot10^{-4}$	$6.3\cdot10^{-3}$	$5.5\cdot10^{-3}$
Kane parameters	**Virgin**	**Implanted**	**Annealed 60 s**
Work function ϕ, (eV)	5.15	5.3	5.1
A, ($eV^2\cdot s$)	$9.5\cdot10^5$	$2.2\cdot10^5$	$6.4\cdot10^5$

TABLE 1. Model parameters for OSEE of thin SiO_2:Ge films.

CONCLUSION

Evolution of the host matrix state of the Si-SiO_2:Ge structure was examined by means of OSEE spectroscopy. Low-energy electron emission is observed under UV excitation in the SiO_2 transparency gap. It is attributed to the surface and interface states, which cannot be distinguished well so far. The electron emission variants of Urbach rule (hv < 5.2 eV) and Kane dependence (hv > 5.2 eV) were used to approximate OSEE spectra. In both cases, the optical absorption stage determines the electron emission processes. The correlation observed between parameter values suggests the validity of Urbach- and Kane-related models. The dominating role of static atomic disorder during the ion implantation and flash annealing was established. Obtained value of power factor n = 2 suggests the major contribution of indirect optical transitions to the processes of OSEE excitation.

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