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Time dependence of silica optical properties during the implantation of fast hydrogen ions: Experiment

O. Kalantaryan [a], V. Zhurenko [a,*], S. Kononenko [a], E. Barannik [a], O. Kononenko [b]

[a] V. N. Karazin Kharkiv National University, Kharkiv, Ukraine
[b] CERN, Geneva, Switzerland

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ABSTRACT

The luminescence technique has been applied to study long-time hydrogen ion implantation of silica. It was found that the changes of the spectrum shape for the luminescence radiation are caused by diffusion of hydrogen from the implanted layer. Analysis of the luminescence radiation spectra showed that hydrogen passivated the non-bridging oxygen hole centers (HBOHCs) and modified the oxygen deficiency centers (ODC).

As the absorption dose grows a different behavior of luminescence in the blue (maximum at 456 nm) and the red (maximum at 645 nm) bands is demonstrated. Luminescence radiation intensity associated with the ODCs increased during the implantation due to the growth of modificated ODC's contribution. At the same time luminescence radiation intensity associated with NBOHCs had a non-monotonic dependence on the absorption dose.

On the basis of our theoretical model and the experimental data, we calculated the average radiation-enhanced diffusion coefficient of hydrogen, the product of average value of the cross-section of the radiation defect creation and the initial portion of defects and the reaction rate constant for non-bridging oxygen passivation by the hydrogen.

1. Introduction

Interaction of ions, electrons as well as X-rays with dielectrics and semiconductors is accompanied by luminescence. Spectrum shapes for cathodo- (see, for example [1–4]), iono- [5–8]), neutron- [9] and radioluminescence [10] are different, but generally have a two-band structure in the visible wavelength range.

Silica luminescence has been widely studied over the decades due to the important material properties in many technical applications. The difference of ion bombardment from other types of luminescence radiation excitations is high energy losses [11], for example, in comparison with electrons of the same energy [12]. Understanding of ionoluminescence is impossible without the conception of radiation phenomenon for luminescence centers and excitation energy. There are two main bands in the visible wavelength range of silica spectrum: a blue band with a maximum near to $\lambda = 456$ nm and a red band — $\lambda = 645$ nm. It is reasonable to note that the blue band ionoluminescence intensity is considerably larger than the one for the red band. The red band corresponds to the non-bridging oxygen hole centers (NBOHC) (see, for example [1,13]. The blue band is associated with the oxygen deficiency centers (ODC) (see, for example [2,6,14]) and emission from recombination of self-trapped excitons (STE) [6,15,16]. ODC is a common term for different defects with oxygen deficiency. These are E'-centers (in silica any center comprising an unpaired spin in a sp^3-like orbital of a 3-fold-coordinated Si atom: oxygen vacancy [17,18], threefold coordinated silicon [1,17]), twofold coordinated silicon [19].

STE in silica leads to defect creation in about of 1% cases or light generation in blue band (by recombination of STE) [20,21]. Defects violate exciton states, and can act as sites that activate the recombination of the excitons [5,22,23]. Intensity of ionoluminescence radiation is a product of ionization loss and defect profiles in a solid [22,23].

Hydrogen implantation is a technology in general use. It significantly affects the spectra of silica luminescence [24,25] and can be explained by the change of balance between the defect formation, modification and passivation. Moreover, probability of the defect excitation and subsequent light radiation plays an important role. Presence of implanted hydrogen in silica changes conditions of the luminescence radiation (LR) generation [24]. Hydrogen can be

* Corresponding author.
E-mail address: v.zhurenko@gmail.com (V. Zhurenko).

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considered as an important impurity because it is chemically active. It can saturate oxygen dangling bond NBOHC (≡Si—O·), the threefold-coordinated SiO_2 defect – ODC or the E'-center (≡Si·) through the chemical reactions:

$$\equiv Si - O^{\cdot} \text{ (or } \equiv Si^{\cdot}) + H\circ \rightarrow \equiv Si - OH \text{ (or } \equiv Si - H), \quad (1)$$

where ≡ denotes the three bonds and "·" represents an unpaired electron [1,12].

Layer of implanted hydrogen in a sample becomes wider due to diffusion during the long-time irradiation of silica. The term long-time irradiation means that diffusion flux of hydrogen reaches the surface of the sample [26]. As a result implanted hydrogen ions occupy the entire luminescence area. Hydrogen diffusion mechanisms can be of a thermal or a radiation-enhanced nature. At a room temperature the thermal diffusion coefficient for silica is 10^4 times less than in the radiation-enhanced case [27]. High temperatures (more than 700 °C) are required for thermo-diffusion coefficient to become observable [28].

This paper deals with the influence of hydrogen diffusion on silica luminescence spectrum shapes during a long-time irradiation. Luminescence technique permits to investigate hydrogen diffusion processes by studying the spectrum shape. Using a mathematical model developed in [29] we found an influence of hydrogen on both of the luminescence centers (ODCs and NBOHCs). Here we present some of the experimental results for atomic and molecular hydrogen implantations of silica determining the features of the defect creation dynamics at different implantation stages. The dose dependence of the spectral shape corresponded to the time dependence at constant ion flux. Based on these results a theoretical model is suggested and a quantitative estimation of diffusion process in silica is performed. Various parameters, for instance a cross-section of the defect formation, are calculated and presented in the paper.

2. Experimental setup

In the experiments we have used a fused quartz specimens of kV-type with the OH-group contents larger than 150 ppm (analogies H-Vitreosil England, T1030 Japan) and the polished plane-parallel plates 16 × 16 × 1 mm^3 as the targets. 210 keV per a.m.u. hydrogen ion implantations have been carried out employing the Van de Graaf accelerator at the angle of 30° with respect to the surface normal. Current density ranged from 0.3 to 0.6 μA/cm^2 during the implantation stage and 0.1 μA/cm^2 at the stage of the luminescent spectrum measurements. Maximum implantation fluence was up to 6 × 10^{17} cm^{-2}. Both the molecular and atomic hydrogen ion beams of 210 keV per a.m.u. were used for the implantation. 420 keV H_1^+ beam was used only for the LR excitation from the sample implanted by hydrogen.

LR was measured from the irradiated spot of the surface at the different observation angles β and was registered by grating monochromator with photomultiplier. LR spectra were corrected by a spectral sensitivity of the optical channel and were normalized to the corresponding beam current. More details about the experimental setup can be found in [30].

Hydrogen implantation was cyclical. Every cycle consisted of two stages (see Fig. 1).

At the first stage we measured LR induced by the ion beam with a low current density at observation angles of 0°, 30°, 45° and 60°. Implantation dose was accumulated with the higher current density at the second stage. The total implantation dose of a cycle was a sum of all the doses accumulated at the both stages. Maximal absorption dose was 4.35 × 10^{10} Gy (3 × 10^{21} particles per cm^3).

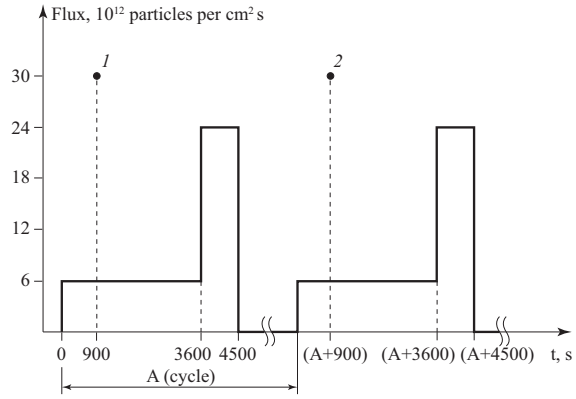

Fig. 1. Time dependence of the silica implantation process (points 1 and 2 correspond to the ends of the LR measurements, $\beta = 0°$).

3. Results

Kinetic energy of ions is an LR energetic source. Energy lost by the fast ions with the velocity $v_1 \gg v_0$, where v_0 is the Bohr velocity, is transferred mainly to the electron subsystem of solid. Ionization losses and defect concentration define the LR intensity at every single point of the ion track [5,22,23]. The total LR spectrum is an integral over all the tracks since the silica is transparent at the visible wavelength range.

3.1. SRIM-simulation

We have also performed a simulation using the SRIM–TRIM software [10] to understand the processes taking place in a sample under the implantation. It is widely used software for calculation depth profiles and energy losses for ions. For example, the implanted profiles in silica experimentally studied by the Rutherford backscattering technique were in a good agreement with SRIM–TRIM simulations [31]. We carried out the simulation at the beginning of a dose accumulation excluding hydrogen diffusion. According to [32], properly taking diffusion into account widens the ion-implanted depth distribution.

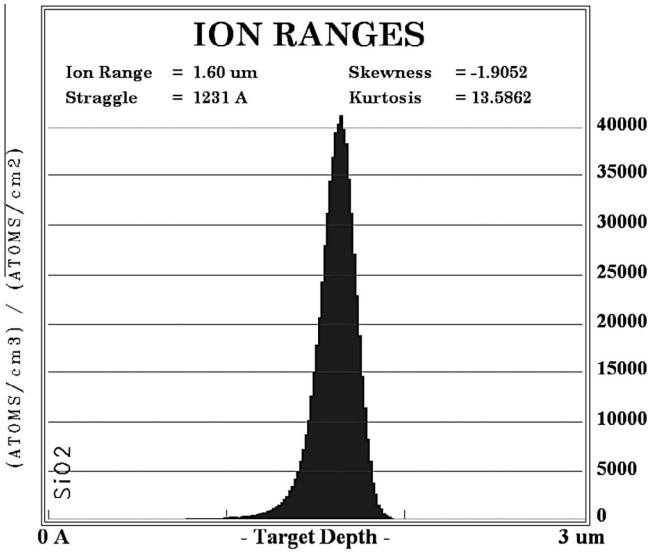

Fig. 2. Distribution of implanted 210 keV per a.m.u. hydrogen ions on a sample depth ($\alpha = 30°$) calculated by SRIM–TRIM [11].