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Change of silica luminescence due to fast hydrogen ion bombardment

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Abstract. This paper deals with the luminescence of silica (KV-type) induced by beam of hydrogen ions with the energy of 210 keV per nucleon. An average implantation dose of up to 3.5×10^{21} cm^{-3} (5×10^{10} Gy) was accumulated during irradiation over an extended period. The luminescent spectra consisted of the blue band (maximum at 456 nm) and the red band (650 nm) in the visible range. It was shown that increase in the absorption dose had an effect on the silica luminescence. It was found that the most significant changes in the spectrum occurred during the dose accumulation in the region of 550–700 nm. The shape of the spectrum of the luminescent radiation in this wavelength range was affected both by the oxygen deficient centres (blue band) and non-bridging oxygen hole centers (red band). Mathematical processing of the experimental spectra permitted to identify contributions to the luminescent radiation coming from both types of defects.

Key words: luminescent spectrum • absorption dose • ion implantation • silica

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Introduction

Optical diagnostics are commonly used for measurements of plasma parameters in thermonuclear devices (see, for example [1]). Silica is a prospective material for optical channels of thermonuclear devices and facilities (windows, light guides etc.). Its optical properties can be significantly changed during the operation of the above-mentioned facilities, especially in the future thermonuclear reactor (for which the operation time will be 30 years or more). Intense irradiation by different projectiles from the active zone of the thermonuclear reactor is the main reason for the change of optical properties of the transparent elements [2].

The intrinsic defects such as oxygen-deficiency, oxygen-excess, and dangling bonds define the optical properties of silica in the visible and near UV range [3]. The spatial density of these defects is changed by irradiation. Ions produce defects of higher density in comparison to electrons and gamma-quanta of the same energy. In the case of proton bombardment, an accumulation of chemically active hydrogen occurs. This results in a shift of defect balance because of hydrogen passivation process. The implanted hydrogen can saturate oxygen dangling bond defects [4]. A prolonged irradiation leads to substantial changes of light generation and absorption in the visible wavelength range. These changes are associated with the balance of creating, annealing and passivation of oxygen deficient centres (ODCs) and non-bridging

oxygen hole centers (NBOHCs) [5]. The shape of the spectrum of luminescent radiation (LR) is not altered at an absorption dose of more than 3×10^{21} cm^{-3}, which is the critical dose [6].

Since the energies of hydrogen isotope ions in thermonuclear facilities ranges from hundred eV (neutrals) up to several MeV (thermonuclear protons), we chose 210 keV per a.m.u. hydrogen ion implantation for modeling the behavior of the optical properties of silica under irradiation. In this case no significant morphological changes of the sample surface were observed because the sputtering was negligible. We used both the atomic and molecular ions because the latter made it possible to reduce the dose accumulation time and were more effective in increasing the defect density in the sample.

The energy of luminescent radiation (LR) comes from ionization losses of ions and subsequent defect excitation. It is well known that ion-induced luminescent spectrum consists of two wide bands in the visible wavelength range [7]. The ODCs are the source for the blue band LR (with a maximum at λ = 456 nm), while NBOHCs are responsible for the red band light emission (with a maximum at λ = 645 nm). The defect balance and the shape of the LR spectrum does vary under long time irradiation by hydrogen ions [8].

The main task of our study was to examine the change of the luminescent properties of silica during a hydrogen ion implantation with up to 5×10^{10} Gy absorption dose by means of the ionoluminescence technique. Ionoluminescence is an appropriate technique to investigate microscopic processes accompanying creation of defects and their evolution in the process of irradiation.

Experimental setup

The experiments were performed using a setup described in detail in earlier papers [8, 9]. The silica implantation was carried out with a Van de Graaff accelerator. A silica target was bombarded with a beam of hydrogen ions with the energy of 210 keV per nucleon, at an incidence angle of $\alpha = 30°$. The targets were made from 1 mm thick plane-parallel silica plate (KV-type). The average implantation dose was up to 3.5×10^{21} cm^{-3} (5×10^{10} Gy). The silica implantation and LR measurements were done by means of the same ion beam, but at different current densities. The implantation current density was up to 3 μA/cm^2. Luminescent spectra were measured at reduced beam current density to decrease the influence of the dose accumulation during the spectrum recording cycle. The 420 keV molecular or 210 keV atomic beams had current densities ranging from 0.3 μA/cm^2 to 0.6 μA/cm^2. The observation angle β varied from 0 to 70° by means of a flexible light guide. The LR was collected from whole irradiated surface of the sample independently of the β angle. Measurements of the luminescence spectra were performed in the wavelength range of 400–700 nm by means of a grating monochromator (1200 mm^{-1}, 1.3 nm per mm). A photoelectric multiplier was used as a detector. The spectral sensitivity of the photocathode was $\geq 2 \times 10^{-2}$ A·Watt^{-1} at λ=400 nm; the anode sensitivity was 10 A·lm^{-1} at U = 1.8 kV; the maximal dark current was 6×10^{-10} A at U = 1.8 kV.

The optical channel was calibrated using an incandescent spectrometric lamp. The luminescent spectra were corrected according to the spectral sensitivity. Since the luminescent light was generated at each point of the ion track in silica, the influence of the surface contamination on the optical spectra was negligible.

Results and discussion

The implantation was performed over a long time (several tens hours). Moreover, we used different species and energies of ions. The LR spectra were measured at different observation angles. In order to compare the spectra obtained in different experiments we carried out a normalization procedure. It was observed that the maximum intensity of the blue band was practically unchanged for absorption doses exceeding 2.4×10^8 Gy. This fact allowed for normalization of the LR spectra on the blue band maximum for the subsequent mathematical treatment.

The LR normalized spectra at the beginning and end of the implantation process are shown in Fig. 1. It was found that a most pronounced change of the spectral shape occurred at 550–700 nm wavelength

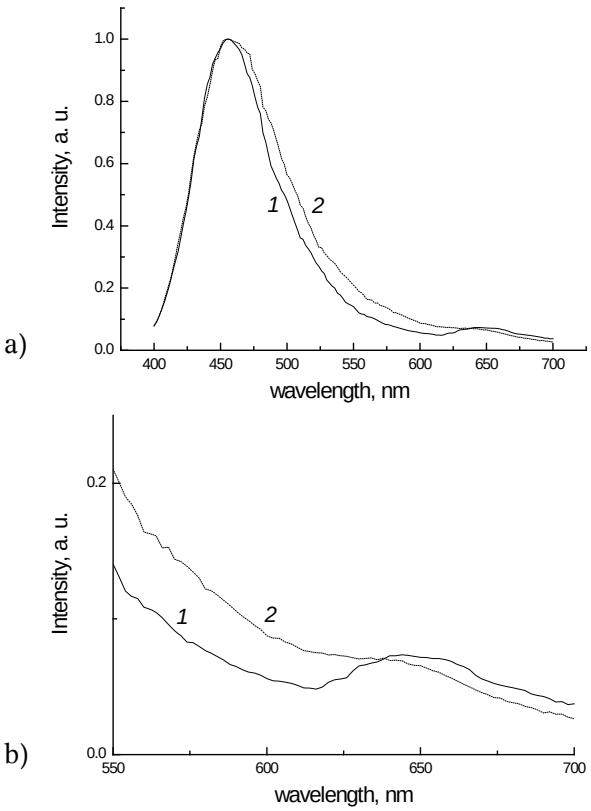

Fig. 1. The LR spectra induced by a beam of 210 keV H^+ ions, recorded at different stages of the ion implantation (β = 0°): 1 – at the beginning; 2 – at the end, with the absorbed dose 3.5×10^{21} cm^{-3} (5×10^{10} Gy). a) – The full spectra; b) – the wavelength region where the spectrum change is the largest (the scale is enlarged).

arange (see Fig. 1b). Hereinafter we consider the 550–700 nm wavelength range.

We think that both the blue and the red bands made the contributions to the LR in this wavelength region. The maximum intensity in the blue band was significantly greater than in the red band. It was reasonable to expect that the in the blue band the LR would spread up to 700 nm. On the other hand, the red band LR intensity was smaller than the intensity of the long-wavelength wing of the blue band in the spectral range below 600 nm. The region of a maximal change in the spectrum (see Fig. 1b) consisted of two subregions: up to 590 nm – the blue band prevalence, and 600–700 nm – a sum of comparable intensities from both bands. We performed the mathematical processing of the normalized spectra to determine the contributions from each type of defects.

Analysis of the LR data showed that the experimental spectra at the wavelength range 490–590 nm could be approximated with high accuracy by the function $K(\lambda) = e^{a+b\lambda}$, where a and b are empirical coefficients, and λ is the wavelength (in nm). In the absence of optical features in the range of 456–700 nm, there is no reason to assume that the functional relationship will be changed (if we consider only the radiation from this type of defect). It is thus reasonable to assume that the LR (associated with ODCs) is described by $K(\lambda)$-function not only in the wavelength range 490–590 nm, but also up to 700 nm. This assumption let us to identify the influence of ODCs and NBOHCs on the total LR in the 600–700 nm range. We determined a and b coefficients for each spectrum and found LR (associated with NBOHCs) by $K(\lambda)$ subtraction from the experimental spectrum. As a result we obtained separated blue and red bands (see Fig. 2) and found the contributions from both types of defects, namely ODSs and NBOHCs, to the LR in the wavelength range being studied.

In Figs. 3 and 4 we show the dependence of the shape of the spectra for, correspondingly, ODSs and NBOHCs on the absorption doses in the case of H^+ implantation and $\beta = 0°$. The analogous results were observed for different β angles. In the case of H_2^+ implantation the dose dependence had a similar behavior.

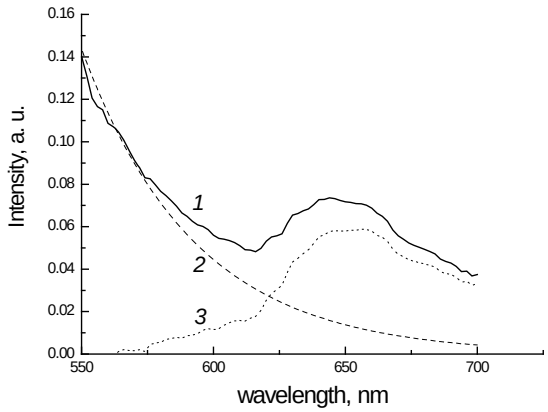

Fig. 2. The LR spectra induced by a beam of 210 keV H^+ ions at the beginning of the ion implantation ($\beta = 0°$): 1 – the experimental curve; 2 – the calculated $K(\lambda)$ curve (blue band); 3 – the calculated red band curve.

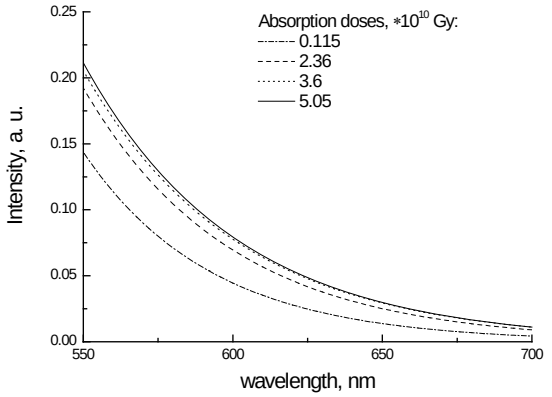

Fig. 3. The calculated LR blue band spectra $K(\lambda)$, for different values of the absorbed dose (210 keV H^+, $\beta = 0°$).

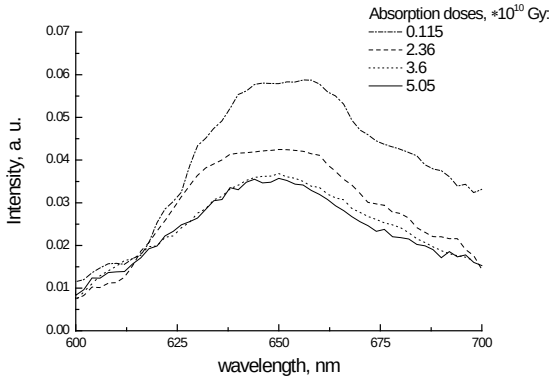

Fig. 4. The calculated LR red band spectra, for different values of the absorbed dose (210 keV H^+, $\beta = 0°$).

The long-wavelength wing of the blue band significantly increased with the growth of the absorption dose (Fig. 3), and at the same time the red band intensity decreased (Fig. 4). As a consequence the red band became virtually indistinguishable on the blue band background (see Fig. 1 curve 2). This occurred at the absorption doses above the critical one. But the mathematical treatment revealed that the red band LR made appreciable contribution to the total LR in this wavelength region. The influence of chemically active implanted hydrogen on NBOHCs brought to passivation of these defects.

Three processes defined the evolution of the spectrum shape in the blue and the red band: 1) production of ODCs and NBOHCs; 2) annealing of the defects; 3) defect modification as a result of chemical activity of hydrogen. At the beginning of hydrogen implantation the production of NBOHCs was predominant. Further increase of the implantation dose led to partial passivation of NBOHCs by hydrogen. Starting with a certain dose the passivation of NBOHCs by hydrogen became considerable. The balance between passivation and production of NBOHCs was shifted. For absorbed doses exceeding the critical value (4×10^{10} Gy) the dynamic equilibrium between the three above-mentioned processes was reached. On the other hand, modification of the ODCs by implanted hydrogen resulted in an increase of the intensity of the blue band long-wavelength wing. The critical dose was defined as threshold, and the luminescent spectrum shape remained unchanged for absorption dose above critical one.

Conclusions

It was shown that the growth of the absorption dose influenced the luminescent properties of silica, namely the LR spectrum. Both ODC and NBOHC defects had influence on the LR spectrum shape at the wavelength range of 550–700 nm. Accumulation of implanted hydrogen in silica led to the passivation of NBOHCs, and, consequently, the intensity of the red band intensity decreased. At the same time the intensity of the blue band increased at mentioned above wavelength range. A dynamic equilibrium between the defect production, annealing and passivation was reached for absorption doses exceeding the critical value. Consequently, further irradiation did not result in the change of the silica LR spectra.

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References

1. Costley, A. E., Sugie, T., Vayakis, G., & Walker, C. I. (2005). Technological challenges of ITER diagnostics. *Fusion Eng. Des*., *74*, 109–119. DOI: 10.1016/j.fusengdes.2005.08.026.
2. Gonzalez, S. M., Morono, A., & Hodgson, E. R. (2005). Optical and electrical degradation of H^+ implanted KS-4V quartz glass. *Fusion Eng. Des*., *74*, 831–834. DOI: 10.1016/j.fusengdes.2005.06.191.
3. Cannas, M., Vaccaro, L., & Boizot, B. (2006). Spectroscopic parameters related to non-bridging oxygen hole centers in amorphous-SiO_2. *J. Non-Cryst. Solid*, *352*, 203–208. DOI: 10.1016/j.jnoncrysol.2005.12.001.
4. Salh, Roushdey, & Fitting, H. -J. (2007). Mechanism of radiation-induced defects in SiO_2: The role of hydrogen. *Phys. Status Solidi (c)*, *4*(3), 901–904. DOI: 10.1002/pssc.200673717.
5. Kalantaryan, O. V., Kononenko, S. I., & Zhurenko, V. P. (2013). Ionoluminescence of silica bombarded by 420 keV molecular hydrogen ions. *Funct. Mater.*, *20*(4), 462–465.
6. Kalantaryan, O. V., Kononenko, S. I., & Muratov, V. I. (2000). Distance-monitoring of absorption dose on materials under ion irradiation. *Plasma Fusion Res*., *3*, 274–276.
7. Jaque, F., & Townsend, P. D. (1981). Luminescence during ion implantation of silica. *Nucl. Instrum. Methods*, *182/183*, 781–786.
8. Kononenko, S. I., Kalantaryan, O. V., Muratov, V. I., & Zhurenko, V. P. (2007). Silica luminescence induced by fast light ions. *Radiat. Meas*., *42*, 751–754. DOI: 10.1016/j.radmeas.2007.02.061.
9. Kalantaryan, O., Kononenko, S., Zhurenko, V., & Zheltopyatova, N. (2014). Fast ion induced luminescence of silica implanted by molecular hydrogen. *Funct. Mater.*, *21*(4), 26–30.