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

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ABSTRACT

Formation, excitation and passivation of defects by absorbed hydrogen have been extensively reported in the literature. Here we present a basic luminescence-diffusion model to simulate creation and chemical annealing behavior of non-bridging oxygen hole centers in silica by their treatment under a long-time hydrogen implantation. The model is in a good agreement with experimental data and explains the uncommon nonmonotonic time dependence of the non-bridging oxygen hole centers luminescence during the hydrogen implantation. The proposed model establishes the quantitative relation between the intensity dependence of luminescence on its intrinsic diffusivity, hydrogen concentration, defect concentration and cross-section of their creation. Possibilities to estimate these parameters based on the experimental data for the efficiency of silica luminescence are also discussed.

1. Introduction

Balance of hydrogen in silica is very important for fabrication of optical fibers and modern interfaces [1]. Hydrogen saturation of silica can be performed by both implantation and thermodiffusion under hydrogen gas exposure of the sample.

There are a number of up-to-date models for formation, excitation and passivation of defects by absorbed hydrogen. The corresponding thermodiffusion process through the surface of bulk silica has been studied in [2] at different temperatures. Hydrogen can easily diffuse through the glass, however due to the reaction with the defect centers its effective o is smaller than the intrinsic one at the given temperature. The explanation of the experimental data has been also performed in [2] by solving the complete reaction–diffusion problem based on the hydrogen diffusivity, defects and hydrogen concentrations. In this case new defects are not formed and a chemical annealing of the existing defects is occurred. Let's note that the hydrogen implantation differs from the Tandon case of hydrogen gas exposure.

Along with the other methods ion implantation technique is widely used to develop novel functional materials based on silica [3]. D. Fink et. al. studied hydrogen diffusion induced by ion implantation by a special Nuclear Reaction Analysis often referred to as the "1 s N technique" [4]. The hydrogen implantation profiles were also measured in [4] and the hydrogen diffusion coefficients were calculated with «DIFFUS» code on the basis of the measured profiles.

The implantation is accompanied by formation, excitation and annealing of the defect structure in the matter. The defects can affect the performance of modern silica technologies (microelectronic devices, optical fiber communications and others) [2 and the references there in]. In particular, the understanding of radiation effects in silica-based materials is all-important for optical functional applications of materials [5].

Silica optical properties are to a considerable degree depend on the concentration and profile of different defect type [6]. It is well known that there are two types of intrinsic silica defects: ODC (oxygen deficiency center) and NBOHC (non-bridging oxygen hole center) (see [6] for example). It has been determined that in the visible spectrum range ODC and NBOHC are luminescent light source reaching the maximum intensity at 460 nm (2.7 eV) and 645 nm (1.9 eV), respectively.

According to [7,8] the hydrogen ion implantation changes luminescent spectra. At the present time, large experimental data array for defect formation under the ion beam exposure and concomitant ionoluminescence in silica has been obtained and models for defect

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formation and luminescent light generation have been suggested [9–11]. Defect formation occurs along the entire ion track resulting in luminescent light generation under the ion bombardment. Dynamics of luminescence efficiency are quite various at different regions of silica sample due to the opposite processes of defect formation and annealing. The chemical annealing of the oxygen hole centers by reacting them with hydrogen results in the formation of hydroxyl having a different absorption wavelength in comparison to NBOHC.

Luminescent light spectrum changes are associated with a defect balance taking into account hydrogen diffusion through the sample. In our case this diffusion toward the surface of the sample has radiation-enhanced character with diffusion coefficient larger than the one for the thermal case [4] especially for the higher absorption doses. Luminescent spectrum treatment not only permits to separate an influence of the defect on the luminescent spectrum, but also to obtain luminescent temporal characteristics under a long-time irradiation [12].

Long-time irradiation by the hydrogen ion causes changes in the luminescent radiation spectra of silica [5,9,13]. It was found, that the luminescent bands responsible for ODCs and NBOHCs change in different ways under a long-time irradiation since the implanted hydrogen ions interact with these defects in different ways. As mentioned above, several processes take place: not only the formation and excitation, but also modification and passivation of defects. These processes are closely connected and should be studied by solving the complete system of luminescence-diffusion equations. To determine the relation between luminescent radiation (LR) and defect formation processes one can use the model [8] for instance.

In this paper we develop a model of LR temporal changes associated with the cross-sections of the above-mentioned processes and a hydrogen diffusion from the implanted layer. By solving the complete luminescence-diffusion problem, we are looking to explain the experimental data and the uncommon nonmonotonic time dependence of luminescence during the hydrogen implantation observed in [14]. We also determine parameters, which can be estimated based on the LR time dependence for different combinations of defect concentration and the hydrogen ions flux density.

2. Theoretical models and results

2.1. Dynamics of hydrogen implantation

We consider the time dependence of hydrogen atoms concentration $n_H(\vec{r}, t)$ during the implantation process. As noted in [4], in the case of low temperature and low-fluence implantation the depth distributions of energetic ions implanted into solids are accurately determined by the dedicated computer codes like SRIM/TRIM [15]. At high fluence implantation the secondary effects such as radiation enhanced mobility become important and lead to same deviations from the well-known distributions [4]. As a result, the dynamical equation for time dependence on hydrogen concentration should contain two major terms. The first one is to describe the initial local accumulation of hydrogen atoms in the sample of silica and the second one to account for their simultaneous diffusion. In the most simplified model of the one-dimensional implantation, which agrees well with experiments in [7], the proper dynamic diffusion equation can be written in the following form

$$\frac{\partial n_H(x,t)}{\partial t} = D_H \frac{\partial^2 n_H(x,t)}{\partial x^2} + (2\Delta R_p)^{-1} \phi [\theta(x - R_p + \Delta R_p) - \theta(x - R_p - \Delta R_p)], \tag{1}$$

where x is the coordinate along the ion beam axe, D_H is the diffusion coefficient of hydrogen, ϕ is the flux density of ions, $\theta(x)$ is the Heaviside function and ΔR_p is the width of initial hydrogen distribution so that the region of initial hydrogen accumulation due to the implantation is defined by the two-sided inequality

$$R_p - \Delta R_p \leqslant x \leqslant R_p + \Delta R_p.$$

Taking into account the well-known ratio [4,16]

$$\Delta R_p / R_p \ll 1, \tag{2}$$

which is satisfied for high-energy ions, the realistic distribution profile can be neglected and is replaced by the difference of the Heaviside functions [11] giving the uniform distribution in the region of initial localization, as shown in Fig. 1a.

For hydrogen implementation (1) is a subject to the initial and boundary conditions as follows:

$$n_H(x, 0) = 0, \tag{3}$$

$$n_H(x,t)|_{x=0} = 0, \quad \partial n_H(x,t)/\partial x|_{x=R_p+\Delta R_p} = 0. \tag{4}$$

We assume here that the ions are implanting through the sample surface with coordinate $x = 0$, at which the concentration of hydrogen is constantly zero due to vaporization. The boundary conditions can also be simplified at $x = R_p + \Delta R_p$, where the flux of hydrogen is negligibly small since the radiation-enhanced diffusion coefficient D_H is very large in comparison with the one of the thermal hydrogen mobility in the area $x > R_p + \Delta R_p$. In other words, the leak of the hydrogen into the unirradiated area is very small, as it is proved below.

Conditions (3) and (4) result in the following solution of Eq. (1) [17]:

$$n_H(x,t) = \sum_{n=0}^{\infty} \left[\int_0^t e^{-D_H \left[\frac{\pi}{2(R_p+\Delta R_p)}\right]^2 (2n+1)^2 \tau} f_n d\tau \right] \sin \frac{\pi(2n+1)}{2(R_p + \Delta R_p)} x, \tag{5}$$

where

$$\begin{aligned} f_n &= \frac{1}{R_p + \Delta R_p} \Delta R_p^{-1} \phi \int_0^{R_p+\Delta R_p} [\theta(x - R_p + \Delta R_p) - \theta(x - R_p - \Delta R_p)] \\ &\quad \times \sin \frac{\pi(2n+1)}{2(R_p + \Delta R_p)} x dx \\ &= \frac{1}{R_p + \Delta R_p} \Delta R_p^{-1} \phi \int_{R_p-\Delta R_p}^{R_p+\Delta R_p} \sin \frac{\pi(2n+1)}{2(R_p + \Delta R_p)} x dx. \end{aligned}$$

Due to the strong inequality (2) the coefficients f_n can be rewritten as

$$f_n = \frac{2}{R_p} \phi \sin\left(\frac{\pi}{2} + \pi n\right) = \frac{2}{R_p} \phi (-1)^n. \tag{6}$$

Substituting (6) into (5) and performing the integration with respect to τ gives

$$\begin{aligned} n_H(x,t) &= \frac{2\phi}{R_p D_H} \sum_{n=0}^{\infty} (-1)^n \left[\frac{2R_p}{\pi(2n+1)}\right]^2 \\ &\quad \times \sin \frac{\pi(2n+1)}{2R_p} x \cdot \left[1 - e^{-D_H \left(\frac{\pi}{2R_p}\right)^2 (2n+1)^2 t} \right] \end{aligned} \tag{7}$$

As follows from the Eq. (7), the general dependence of the hydrogen distribution on time of the implantation t is exponential and in the considered case the diffusion time scale can be defined as

$$t_D = D_H^{-1} \left(\frac{2R_p}{\pi}\right)^2. \tag{8}$$

In accordance with (7) the flux density of ions governs only the magnitude of the hydrogen distribution. For $t \gg t_D$ the final distribution can be obtained directly from the Eq. (7):