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# THE SILICA AND SILICON LUMINESCENCE INDUCED BY FAST HYDROGEN IONS.

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The results of silica and silicon luminescence induced by hydrogen ions bombardment with energy 0.2 ÷ 0,45 MeV and 0.8 ÷ 2.4 MeV were presented in this paper. It was obtained that the ionluminescence spectra of $SiO_2$ were changed under hydrogen ions bombardment essentially. The relation between light intensity and implantation dose was determined. The silicon spectra were measured in the near ultraviolet and visible regions of wavelength. The spectra consist of three wide bands. The band with maximum at 326 - 328 nm was not observed earlier. The mechanisms of generation of these bands are discussed. The possibilities to discover oxide layer formed by the natural way on a silicon surface are shown. The novel method for control of proton dose in quartz was proposed.

## 1. Introduction

It is well known that charged particle beam bombardment of different materials is accompanied by electromagnetic radiation. The projectile energy are spent at two alternative correlated channels, namely, luminescence generation and creation or annealing defects in the sample. The some properties of substance are changed in this case. These changes are determined by forming and annealing of different types of defects and setting a dynamic equilibrium of these processes in the samples. [1,2]. The intensity of these processes increase by ion irradiation of the sample essentially. Moreover, in this case the situation is complicated because ions have the nuclear cross-section more significantly than other particles. The parameters of ionluminescence are unique channel of obtaining of an information about an absorption dose and sample properties.

In modern science and technology the some materials are widely used under high irradiation conditions. It took place at the manufacture of ion implanted semiconductors, in the space, in a active region of nuclear reactors, in the accelerators, etc.. The commonly used materials for microelectronic are silica and silicon. These materials are jointly used for producing MOS-structures ( metal - oxide - semiconductor ). The results of investigations of these material ionluminescence are presented in this paper.

In visible region the luminescence spectra of silica ( induced of different sources) consists of two wide bands (see, for example, [3]). The first band maximum was situated near 455 nm wavelength. This radiation was connected with one of intrinsic silica defects, namely, E′-centers [4].The second band has maximum which was near 645 nm. Its nature are determined another intrinsic silica defects as non-bridging oxygen centers [5]. The optical properties of silica were significantly changed by means of hydrogen present in sample. It was shown in [6] that absorption of light bands with maximums at 4,75 eV and 2,0 eV was essentially decreased by implanted hydrogen. Usually this absorption bands were related with non-bridging oxygen centers.

In the previous investigations [1-3] the silica luminescence was studied for irradiation doses less than $10^{21}$ keV/cm$^3$ and fixing wavelength only. It is necessary to emphasize that the luminescence was investigated from previously irradiated sample by different particles and was excited by ultraviolet sources at majority carried out experiments.

There is a considerable amount of experiments devoted to the research into silicon luminescence. Most of them study the radiation spectra of the sample in the infrared region of wavelength using photoluminescence methods [7 - 12]. The spectra consisted of the selfluminescence band in the range from 1.08μm to 1.27μm (1.15 - 0.96 eV) and from some narrow lines. The authors of those articles explained the generation of these lines by the presence of admixture centres and some defects formed by preliminary forces upon the sample (irradiation by ions [7,10], electrons [8,9] neutrons and γ-quanta [12], temperature annealing, cleavage [13]).

The structure Si - $SiO_2$ is one of the most important objects of experimental research because it is widely used in the electronic industry. It is usually created by different ways of silicon oxidation. The thickness of dioxide film is usually from some ten to hundred nm. Photoluminescence [14], cathodoluminescence [15 - 17] and electroluminescence [14, 18, 19] spectra of these samples consist of some wide bands with their maxima at the wavelength of 650 nm (1.9 eV), 540 - 550 nm (2.3 - 2.2 eV), 460 - 450 nm (2.7 - 2.6 eV) and 280 - 290 nm (4.4 - 4.3 eV). A number of mechanisms of generating these bands has been proposed.

Particularly the radiation at the maximum at 650 nm is explained with the center of nonbridge oxygen in the dioxide film. The radiation at the maximum 460 - 480 nm is connected with the shortliving defect recombination such as split silicon-oxygen bonds in $SiO_2$. At this time there are some other models of the luminescence centres. This paper presents the results of different materials luminescence induced by fast light ionbombardment in the near ultraviolet and visible regions of wavelength. There are silica and silicon samples in our investigation. The experimental results of study of luminescence spectra of silica during ion bombardment by implanted doses up to $10^{24}$ keV/cm$^3$ were obtained. The relation between ionluminescence silica spectra parameters and absorption doses was investigated. Investigation of the possibilities to discover oxide layer formed by the natural way on a silicon surface are shown.

## 2.Experiment

The measurements of the luminescence induced by ion bombardment of the different targets were carried out using the setup described in detail in [20]. The block diagram of this setup is shown at the Fig. 1. Two different Van der Graaf accelerators were used in experiments. The parametres of first accelerator were such as: energies from 0.8 MeV to 2.4 MeV and current density up to 1 μA/cm$^2$ and for second case: the energy range was 210-420 keV and current density was up to 30 μA/cm$^2$. The targets were situated in vacuum chamber **1**. The residual gas pressure up to $10^{-4}$ Pa was maintained by a magnetic-discharge pump. There were targes pure silica and silicon samples of 0.9999 purity (specific resistivity about 1Ω·m were of two kinds: with rough and polished surfaces) in our experiments.The optical radiation from the target surface was pojected by one of two optical channels **2** on the entrance slit of the grating monochromator **3**.

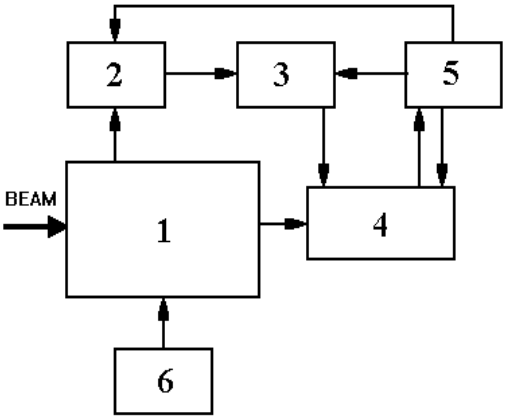

*Fig. 1 The block diagrame of setup*

The first channel consist of the flexible light guide and the quartz condenser. In this case, the samplewas set at the angle 30° with respect to the beam (all angles were measured relatively to the perpendicular to the target surface). The optical radiation was collected by face of flexible light guide under chosen direction. The light from the back of light guide was projected by quartz condenser on the entrance slit of grating monochromator **3**. The observation angle was changed from 0° to 60° by turning of the light guide face in a plate which it perpendicular to the target surface. Detection of the luminescence was performed using a photomultiplier detector in the wavelength region of 400-700 nm. Such experimental scheme permited to change the angle of incedence and the observation angle independently. But sensitivity and spectral range were smaller than of the second optical channel.

For the second channel, the optical radiation from the target surface was pojected by quartz condenser on the entrance slit of the grating monochromator.. The target was put at an angle of 45 with respect to the beam. The axis of the optical system was put at the angle of 90° with respect to the beam. The radiation was studied in the wavelength region 250 to 800 nm.

Detection of light was performed using a photomultiplier detector in the current mode. The obtaining informations arrived to small computer **5** by means interface **4.** Detection and signal processing, control of the all setup system work were carried by this computer **5**. The optical channels of the device were calibrated in respect of the incandescence spectrum-metric lamp **6**. Luminescence spectra were corrected according to the spectral sensitivity and were normalized per the beam current.

## 3.Experimental results and discussion

The typical luminescence spectra of nonirradiated silica under ion bombardment are shown in Fig.2 (curve 1).

This spectra form was earlier observed for pure silica by the different type of excitation [1-3 ]. The most intensive (first) band had maximum at 460 nm . Its presence was connected with E′ - center defects [4]. The second band had the maximum at 650 nm and situated on the long wave wing of the first band. The irradiation in this band was associated with non-bridging oxygen centers [5].

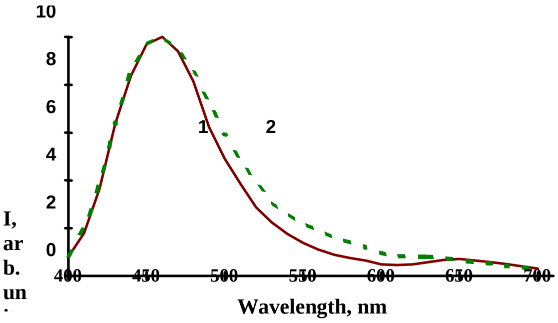

*Fig.2 The ionluminescence spectra of* $SiO_2$ *under proton bombardment : curve 1 - nonirradiated quartz, curve2 - by implanted proton doses of* $3\cdot 10^{21}$ *cm* $^{-3}$*m (* $0.7 \cdot 10^{24}$ *keV/cm* $^{-3}$*)*

The ionluminescence spectra was changed when the proton (or other hydrogen ions - $H_2^+$, $H_3^+$) dose increased. The intensity of the long wave wing of the first band grown ( see Fig. 2, curve 2). The intensity of the short wave wing and maximum were unchanged. The ratio of intensities in the point with wavelength of λ=620 nm to ones at first band maximum increased from $5{,}6\cdot 10^{-2}$ ( nonirradiated silica) to $7{,}3\cdot 10^{-2}$ ( for dose ~ $3\cdot 10^{21}$ cm$^{-3}$). The intensity of second band decreased and became almost indistinguishable on background of the first band. There results were obtained for proton energy of 210 keV. The similar results were obtained for using ion energy and for different observation angles.

The spectra changes were determined by implanting dose. We proposed method for control of absorption hydrogen doses by using of the ratio ***R*** of luminescence intensity at 650 nm to ones at 620 nm. It was obtained that the amount of ***K* = *R/l*,** (where ***l*** was path length of proton in $SiO_2$) was depended only from the hydrogen ion density in the silica sample but was practically independent from projectile energy and observation angles (see Fig. 3 ).

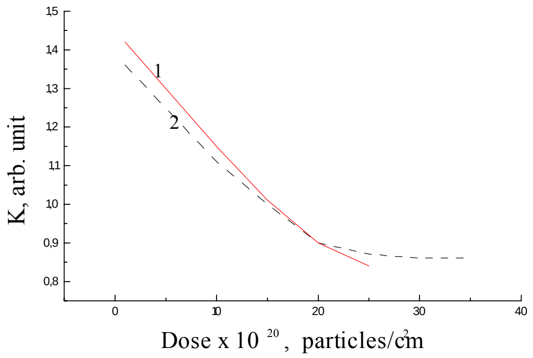

*Fig.3 The coefficient K dependence from proton dose: curve 1 -the proton energy 420 keV; curve 2 - the proton energy 210 keV*

At Fig. 4 are presented the luminescence spectra of the rough (curve 1) and polished (curve 2) samples, while being irradiated by protons with energy of 0.8 MeV.

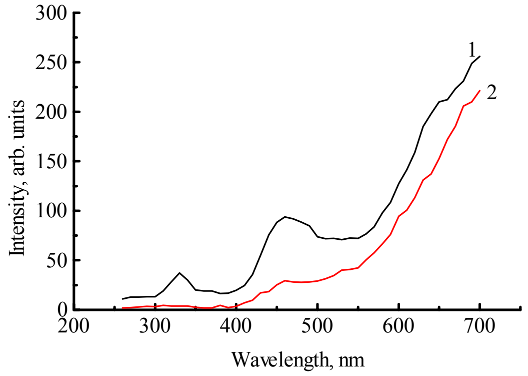

*Fig. 4 The spectra of ionluminescence of silicon induced by 0.8 MeV: 1 - rough sample; 2 - polished sample*

The spectra consist of three wide bands. The most intensive band begins from 380 nm and smoothly increases in the long wavelength side. Increasing the proton energy leads to decreasing light yield in this band for both studied samples. This radiation band is the shortwave border of the silicon selfluminescence which was observed by some authors [7-9]. But this was not observed while researching electroluminescence [14,19] and cathodoluminescence [15 - 17] of Si - $SiO_2$ systems. The radiation intensity in this band slightly depends on the surface condition state though the rough surface increases it. In the wavelength region of about 300 - 700 nm silicon is nontransparant [21]. The calculations based on the optical constants of silicon show that the skin-layer depth in this case does not exceed 30 nm and it is much less than the path of protons with given energy (this path is of the order of $10^{-3}$ cm). Hence radiation yield of these wavelengths we measure is possible only from the narrow surface region. It is known that specific energy losses for protons with given energies E are described by the formula of Bethe [22]:

$$-\frac{dE}{dx} = \frac{2M\pi Z_1^2 e^4}{mE} Z_2 N \cdot \ln\left(\frac{mE}{IM}\right),$$

where $Z_1$, $Z_2$ are charges of a projectile and the target atom correspondingly; e, m are charge and mass of electron, ***M*** is mass of ion; ***N*** is density of target atoms, I is average potential of excitation of target atoms. As we can see from the formula the specific losses decrease with the growth of projectile energy. Hence, increasing the energy of bombarding particles leads to decreasing of the absolute value of energy given by ion to layer where the radiation comes out. As the result the light yield decreases. It was this regularity that we observed in our experiment.

The light band with the maximum at 460 nm (2.7 eV) is clearly seen on the background of the first band and is present in all the spectra of ionluminescence of rough sample. The intensity of this band falls down when the proton energy increases. For the polished sample it is almost indistinguishable at the energy of 2.4 MeV and essentially less than for the rough sample at the energy of 0.8 and 1.6 MeV . The existence of the band with the maximum at 460 nm (see Fig.4.) is the distinctive feature of $SiO_2$ ( to compare with Fig2, curve 1 ). It is connected with the presence of the dioxide film on silicon surface. The generation of radiation with its maximum at 460 nm was observed when the oxide film thickness was more than 40 - 50 nm for electroluminescence or cathodoluminescence investigations [15,16]. In our case the band with its maximum at 460 nm is generated in the oxide film with the thickness of some atomic layers formed by the natural way. The band with maximum at 650 nm was indistinguishable among the others.

The fact that the light yield in this band depends on the surface roughness can be explained with the following two factors. First, rough surface leads to the forming of more thick oxide layer. Second, rough surface increases the efficiency of transforming the excitations which spread in the oxide layer into electro-magnetic wave.

Radiation with its maximum at 326 - 328 nm (~ 3.78 eV) is present in the rough sample spectrum in the whole region of proton energies. The polished sample has such a radiation of essentially less intensity, which was observed clearly only at $E_p$ = 2.4 MeV. Increasing the proton energy leads to the growth of radiation intensity but the band shape was not changed . This radiation has not been observed earlier neither in the Si - $SiO_2$ structures, nor in pure silicon.

The generating mechanism of the band with the maximum at 326 - 328 nm is not clear still. The oxide film cannot be the source of this radiation because quartz has no such a luminescence band while being bombarded by ions. This radiation cannot be bremsstrahlung or transition one. In those cases the optical constants in the given wavelength region must be essentially changed, but it is not observed for silicon [21]. Moreover, the generated radiation must have approximately equal intensities both from rough and polished samples. Taking into account the same reasons we can say that this radiation cannot be induced by interband transitions. Nevertheless we can propouse some mechanism to explain the generation of this band. Probably excitations are generated along the whole ion track. These excitations can easily or with a small attenuation spread in the sample. Reaching the surface this excitation transforms into electromagnetic wave observed by us. This statement is confirmed by two facts. First, intensity is proportional to the ion range length in the substance. Second, the light yield in this band depends essentially on the surface condition state: for a rough sample it is five times higher than for a polished one.

## 4. Conclusion.

It was obtained that the ionluminescence spectra of $SiO_2$ were changed under proton bombardment essentially. The relation between light intensity and implantation dose was determined. The novel method for control of proton dose in quartz was proposed.

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