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In-situ luminescence studies of silica glass during low energy H^+, He^+ and O^+ irradiation

Yingjie Chu[a], Guangfu Wang[a,b,*], Li Zheng[a], Menglin Qiu[a], Peng Yin[a], Mi Xu[a]

[a] Key Laboratory of Beam Technology of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, 100875 Beijing, China
[b] Beijing Radiation Center, 100875 Beijing, China

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ABSTRACT

Silica glass can be used as optical windows of nuclear facilities, optical fibers, and different electronic components in high radiation level environments. The study of structural changes and other effects created by ion irradiation in silica glass is important both for the performance study in above applications and the mechanical study of ion implantation modifications of silica for manufacture advanced materials. A low-energy ion beam induced luminescence (IBIL) set-up was developed at the 200 kV Ion Implanter of Beijing Normal University to measure the dynamic process involved in the damage creation of different materials. In-situ luminescence measurements were performed on silica glasses under the irradiation of 40 keV, 100 keV, 180 keV H^+, He^+ and 100 keV, 180 keV O^+ at room temperature. The evolution of two main emission bands under 100 keV H^+, He^+, and O^+ irradiation was discussed. The IBIL kinetics studied in this work was different to that observed for MeV-ions. The saturated luminescence induced by H^+, He^+ presented almost linear relationship with electronic energy deposition of incident ions. The roles of electronic and nuclear stopping power at different ion energies were discussed to explore the origin of luminescence. Ex-situ optical absorption spectra were measured to monitor optical properties and point defects concentration evolution with H^+ and O^+ fluence.

1. Introduction

Silica glass is widely used in many fields including nuclear technologies, photonics, and microelectronics, and often exposed to high fluxes of radiation. A detailed knowledge of the effect of ionization and atomic collisions under irradiation is required to choose the best candidate from different manufacturing procedures or monitor the functional operation for these optical components. Ions implantation has been applied to understand the generation mechanisms of point defects that affect the optical performance of silica glass [1]. To study structural modifications induced by ion implantation, ex-situ optical techniques like infrared absorption (IR), Raman spectroscopy, and optical absorption were used [2,3]. Compared with above-mentioned methods, ion beam induced luminescence (IBIL) is a very sensitive technique to investigate the luminescent centers associated with structural imperfections and impurities in insulators and semiconductors without interruption of irradiation [4]. Additionally, different ion beam species and energies allow one to vary the probing depth of material compared to other luminescence techniques (cathodoluminescence, photoluminescence, etc.). All of these features make IBIL an in-situ diagnostic technique for the study of the radiation effects that occur during ion irradiation, and an independent means of analyzing defects in both electronic and nuclear energy loss regimes.

Most work focused on radiation damage in silica glasses has been performed with MeV ions [5–11]. The purpose of this study is to discuss the structural effects and differential damage features caused by keV ions. A new IBIL system was successfully developed at the 200 kV Ion Implanter, Beijing Normal University, Beijing, in order to perform in-situ material characterization during low-energy ion irradiation. To investigate the ion species and energies dependence of defects formation near the surface region, silica glasses were irradiated by low-energy H^+, He^+ and O^+. The microscopic radiation damage of irradiated samples was studied by optical absorption to give additional information.

2. Experiment

Fig. 1 shows a schematic diagram of the IBIL experimental setup. The luminescence was collected by a 74-UV collimating lens and transmitted to a compact spectrometer (QEPro, Ocean Optics) through a 600 μm diameter silica optical fiber with a bandwidth of 197–982 nm. The optical fiber was inserted into the vacuum chamber through a

* Corresponding author at: Key Laboratory of Beam Technology of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, 100875 Beijing, China.
E-mail address: guangfu_w@bnu.edu.cn (G. Wang).

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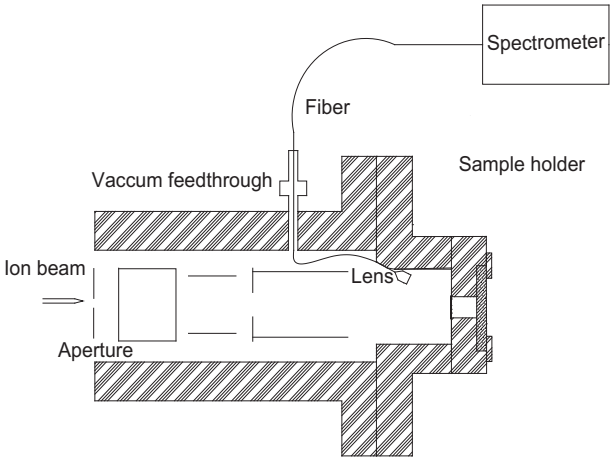

Fig. 1. Schematic of the IBIL setup.

vacuum feed-through. A 100 μm entrance slit was employed to achieve higher light input. The background of experimental setup, mainly including stray light or thermal noise, is subtracted from spectra by the spectrometer before each luminescence measurement. The raw spectral data is not corrected for total instrument response.

Two-sided polished silica samples with a size of 12 × 15 × 1 mm^3 used in this work were commercially available at the China Building Materials Academy, Beijing. The OH content is below 80 ppm and the total metal such as Al, Ti and Fe contents are less than 1 ppm. Ion irradiations were performed with H^+, He^+ at 40 keV, 100 keV, 180 keV and 100 keV, 180 keV O^+ at room temperature. Depth profiles of ions energy loss, in both electronic and nuclear processes, were estimated by SRIM 2013, as shown in Fig. 2. The displacement energy of Si and O atoms is respectively, 15 eV and 28 eV. The sample density is 2.2 g/cm^3. The lattice binding energy of Si and O atoms is 2 eV and 3 eV, with the surface binding energy 4.7 eV and 2 eV. The 40 keV H^+, He^+ and 180 keV H^+ beam current was around 40 μA. The beam current of 100 keV H^+, He^+, O^+ and 180 keV O^+ was 43 μA. For 180 keV He^+, the beam current was 48 μA. The beam homogeneity is within 3.3% controlled by the X, Y plane electric scanning. The scanning area is 4 × 4 cm^2. IBIL spectra were recorded with the integration time 0.25 s for H^+ irradiation, 0.5 s for He^+ irradiation and 0.1 s for O^+ irradiation. The first spectrum was removed to avoid the error caused by asynchronous beam-on and spectra collecting. Optical absorption spectra from 200 nm to 900 nm were measured by an ultraviolet and visible spectrophotometer (Shimadzu UV-365) with a resolution of 0.1 nm.

3. Results and discussion

3.1. IBIL spectra

Fig. 3 shows typical IBIL spectra of silica glasses induced by 100 keV H^+ (a), He^+ (b), and O^+ (c) at a various fluence from 2 × 10^{12} ions/cm^2 to 9.5 × 10^{15} ions/cm^2. The spectra show a broad blue emission band centered at 460 nm (2.7 eV) and a red band peaked at 650 nm (1.9 eV), as well as a quite weak band at 280 nm (4.4 eV), which is too weak to be shown, and will not be further discussed in this work. It is observed that the evolution of luminescence induced by 100 keV H^+, He^+ and O^+ exhibits similar behavior. The luminescence intensity shows an initial rapid growth with fluence, and followed by a slower decrease to a steady level with different evolution rates. The noticeable result is that the luminescence intensity under O^+ irradiation reaches a maximum at a lower fluence around 1.7 × 10^{13} ions/cm^2. In order to compare the emission efficiency under different ions irradiation, the observed luminescence yield is normalized to the integration time and incident beam current. As Fig. 3 (d) demonstrated, the luminescence yield induced by 100 keV He^+ and O^+ is higher than that under 100 keV H^+ irradiation at low fluence. However, the red bands have higher yield under H^+ irradiation than that under He^+ irradiation at the fluence of 8 × 10^{14} ions/cm^2, and 1 × 10^{15} ions/cm^2 for blue. Above a fluence around 3 × 10^{13} ions/cm^2, the emission bands induced by 100 keV H^+ overwhelm O^+ induced luminescence emissions.

In all cases, new point defects are quickly produced at the early stage of irradiation. The peak intensity increases rapidly due to the e-h pairs' radiative recombination with point defects. Low-energy heavy ions irradiation with larger nuclear and electronic stopping power produces more point defects in silica glass than that irradiated by low energy H^+. The probability of e-h pairs trapped in available defects is higher under heavy ions irradiation, thus leading to higher luminescence yield. With the increase of fluence, point defects aggregate and interact with each other into larger defects clusters, converting from luminescent centers into the non-luminescent. The luminescence intensity would reach to a maximum when the radiative recombination rate equals to non-radiative recombination rate. Eventually, the luminescence intensity would decrease to a steady value after the prolong irradiation. For H^+, the lower energy loss leads to smaller number of non-luminescent centers. Therefore, the luminescence intensity during H^+ irradiation is higher than that under heavy ions irradiations at higher fluence.

3.2. Kinetics of luminescent centers

To avoid peak distortion effect during the procedure of spectrum decomposition, IBIL spectra are converted from wavelength signals of $I(\lambda)d\lambda$ versus λ to an energy scale of $I(E)dE$ versus E, so the new intensity$I(E)$ is obtained by multiplying the measured counts $I(\lambda)$ with hc/E^2 [12]. The photo of blue luminescence induced by 180 keV H^+ is displayed, on the inset of Fig. 4. The spectrum is decomposed into four different emission bands by fitting Gaussian functions. These bands and their corresponding origins, reported earlier in literature [5–8,13], are shown in Table 1. The red bands at around 1.82 eV and 1.89 eV can be regarded as a probe for the on-going generation of non-bridging oxygen hole centers (NBOHC, ≡Si−O•) with different precursor states [5,13]. The E′ centers (≡Si•) produce the emission at 2.4–2.5 eV. The emission at 2.71 eV is assigned to e–h pairs' radiative recombination at oxygen-deficient centers (ODC-II, E″ center), corresponding to a triplet-singlet optical transition of ODC-II [11]. The energy variation between E′ and E″ bands is small due to the population of electrons in excited electron levels [6].

All of the above emission bands have been found to be very similar to the reported results, in spite of small differences in peak positions and widths, considering the instrumental factors and Gaussian fitting deviations. The peak positions and FWHM remain nearly the same with fluence except that fluctuations are observed among these four bands at the early stage of irradiation, suggesting the initial superposition of different luminescent centers. The FWHM shown in Table 1 is in agreement with literature [8,13], so it might be caused by electronic energy level splitting or alternative luminescent centers at a neighboring localized energy state.

The normalized luminescence yield evolution of four bands induced by 100 keV H^+, 180 keV H^+, He^+ and O^+ as a function of fluence is shown in Fig. 5. The luminescence yield $Y(\Phi)$ versus Φ can be used to monitor the generation of respective recombination centers under irradiation. The concentration of luminescent oxygen vacancy centers increases to a maximum at around 1.2 × 10^{15} ions/cm^2, and then show a decrease under 100 keV H^+ irradiation. For 180 keV H^+ irradiation, the yield of corresponding centers rises and then gradually reaches to a roughly steady value. Compared with MeV-proton irradiation [8], there is no indication of a maximum in the blue emission yields up to the fluence of 6 × 10^{16} ions/cm^2 for samples with a low-OH content. The explanation for this behavior is that nuclear stopping power takes up a