Kinetics of color center formation in silica irradiated with swift heavy ions: Thresholding and formation efficiency

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We have determined the cross-section σ for color center generation under single Br ion impacts on amorphous SiO2. The evolution of the cross-sections, σ(E) and σ(Sr), show an initial flat stage that we associate to atomic collision mechanisms. Above a certain threshold value (Sr > 2 keV/nm), roughly coinciding with that reported for the onset of macroscopic disorder (compaction), σ shows a marked increase due to electronic processes. In this regime, a energetic cost of around 7.5 keV is necessary to create a non bridging oxygen hole center-E (NBOHC/E) pair, whatever the input energy. The data appear consistent with a non-radiative decay of self-trapped excitons. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4757886]

The effects of swift heavy ion (SHI) beams on dielectric materials (electronic excitation regime) are the cumulative result (overlapping) of disorder tracks caused by individual ion impacts.1–5 In fact, the fluxes used in ion accelerators result (overlapping) of disorder tracks caused by individual materials (electronic excitation regime) are the cumulative...
Silica samples of $7 \times 8$ mm$^2$ and 1 mm thickness, provided by Momentive, have been irradiated at room temperature in the 5 MV tandem accelerator at the Centro de Microanálisis de Materiales (CMAM-UAM), with Br ions (mass number $A = 79$). The energies used as well as the projected ranges and the corresponding nuclear $S_n$ and electronic $S_e$ stopping powers are listed in Table I. Note that the choice of irradiations guarantees a rather constant collision deposition rate but a large span of electronic energy depositions. Ion currents were in the range 10–30 nA to avoid overheating of the samples. The evolution of most abundant color centers (NBOHC, $E_0$, and ODCs, Oxygen Deficient Centers) as a function of irradiation fluence has been monitored through their optical absorption spectra, both in the visible and UV range up to 8.2 eV, where the intrinsic absorption is already relevant. The main parameters used to fit the spectra are given in Table II; in addition to these bands, another one located at 7.3 eV and having a FWHM of 0.65 eV has been included for a proper fitting, following a recent work by Skuja.

A representative optical absorption spectrum of SHI-irradiated silica is shown in Fig. 1(a). The growth curves for all color centers as a function of fluence are Poisson-like,

$$N = N_s \{1 - \exp(-\sigma \phi)\},$$

where $N$ stands for the concentration per unit area, $N_s$ is the saturation level, and $\sigma$ an effective production cross-section. This behavior is exemplified in Fig. 1(b) for one of the irradiation energies (15 MeV). Similar average volume concentrations, $c = N/R_p$ ($R_p$ is the projected range), up to around $10^{19}$ cm$^{-3}$ are reached for all color centers in the surface layer limited by the projected range of the ions. These concentrations are much higher than those obtained under purely ionizing radiation like gamma rays (≈$10^{17}$ cm$^{-3}$, not shown), confirming that new structural precursors are being created by the ion irradiation.

The initial growth rate, $\kappa = (dN/d\phi)_0$, derived from those coloring curves, provides the growth rate, $\kappa = \sigma N_s$, for color center creation; i.e., the number of defects per single ion impact within the damage track. The data for $\kappa$ as a function of the ion energy $E$ and the electronic stopping power $S_e$ are shown in Figures 2 and 3, respectively. Now, we will focus our attention on the NBOHC and $E'$ centers because they have lower data dispersion than the ODC-I centers, which are possibly influenced by edge absorption. The curves show an initial flat stage at low energies (stopping powers) that can be attributed to atomic collision damage in accordance with the nuclear stopping power of the Br ions being essentially independent of energy (see Table I). Above

<table>
<thead>
<tr>
<th>$E$ [MeV]</th>
<th>$S_e (z = 0)$ [keV/nm]</th>
<th>$S_n (z = 0)$ [keV/nm]</th>
<th>$R_p$ [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.09</td>
<td>1.3</td>
</tr>
<tr>
<td>5</td>
<td>2.1</td>
<td>0.06</td>
<td>2.9</td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>0.05</td>
<td>4.5</td>
</tr>
<tr>
<td>15</td>
<td>4.7</td>
<td>0.04</td>
<td>5.8</td>
</tr>
<tr>
<td>25</td>
<td>5.7</td>
<td>0.03</td>
<td>7.6</td>
</tr>
<tr>
<td>40</td>
<td>7.2</td>
<td>0.02</td>
<td>9.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NBOHC</th>
<th>ODC-II</th>
<th>$E'$</th>
<th>NBOHC Extra Band</th>
<th>ODC-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (eV)</td>
<td>4.8</td>
<td>5.8</td>
<td>6.8</td>
<td>7.3</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1–1.2</td>
<td>0.35–0.4</td>
<td>0.8–0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>$F$</td>
<td>0.05</td>
<td>0.15</td>
<td>0.15</td>
<td>0.5</td>
</tr>
</tbody>
</table>

FIG. 1. (a) Gaussian deconvolution of a typical spectrum of irradiated silica and (b) kinetics for the overall density of the various color centers as a function of fluence. The fit to a Poisson law is depicted as solid lines. Both graphics correspond to an irradiation with Bromine at 15 MeV.

FIG. 2. Growth rate of color centers: NBOHC ($\bigtriangleup$), ODC-II ($\bigcirc$), $E'$ ($\Delta$), and ODC-I ($\triangledown$) as a function of the total ion energy. Solid lines are drawn to visualize their evolution. Alternative abscissa scale is the overall e-h pair population per impact.
a certain energy deposition threshold \( S_{th} \) at the surface, \( \kappa \) experiences an approximately linear growth with the total ion energy \( E \) and with \( S_e \), which should be associated to the relaxation of the electronic excitation. At higher energies and stopping powers, the linear rise bends down indicating that other competing processes may become operative. It is noteworthy that the threshold value for coloring obtained from Fig. 3 (around 2 keV/nm) has not been reported so far. It is in good accordance with that determined for the onset of non-radiative excitation in oxides. For \( \mathrm{SiO}_2 \), this mechanism appears strongly supported from some experimental works using irradiation with high energy electrons, x-rays, and laser pulses, although not direct proof is yet available for the case of ion irradiation. Moreover, the non-radiative exciton decay as a mechanism for point defect production in silica and quartz has received strong support from a number of theoretical studies on exciton dynamics and relaxation. The total electron-hole density at \( z \) obtained by integration of expression (2) along \( r \) is usually written in the form: \( N_e(z) = S_e(z)/I \), where \( I \) is an effective ionization energy and \( I \approx 3 \ E_G \) (gap energy). For silica \( (E_G \approx 8 \text{ eV}) \), integration along the whole trajectory yields \( N_e \approx E/(\text{eV}/25) \). For the energies used in our irradiations, this electron-hole density becomes close to the atomic density of the material, suggesting the formation of dense electron-hole plasma. To facilitate comparison, we have included as an additional abscissa axis the total electron-hole density in Fig. 2. It comes out from the figure that the relation \( \kappa \) vs \( N_e \) is approximately linear, indicating that the color center yield per excited \( e-h \) pair is roughly constant, independently of the ion type and energy. A relative constant efficiency of \( \approx 0.1\% \) of the total \( e-h \) population is obtained for the conversion of pairs into color centers, regardless of the temperature reached in the spike. This yield, which refers to exciton formation and self-trapping aside from defect formation, is not far from that found for ion irradiation of alkali halides where the exciton model is well established.

Specific mechanisms that have been proposed for the processes of exciton relaxation in \( \mathrm{SiO}_2 \) are

\( \equiv Si - O - Si \equiv \Rightarrow \equiv Si' + ^1O - Si \equiv \) (3a)
\( \equiv Si - O - Si \equiv \Rightarrow \equiv Si - Si' + O_{(int)} \) (3b)

The first one becomes operative after one-photon absorption of \( \mathrm{F}_2 \) excimer laser light has a quantum efficiency of \( 3 \times 10^{-4} \) and accounts for the similar concentrations of NBOHC and...
\[ \text{Eq. (3b)} \] preferentially occurs at heavily strained bonds, et al. A remarkable finding is that found in our experiments. On the other hand, reaction \( (3b) \) preferentially occurs at heavily strained bonds, which correspond mostly to three- and four-membered rings. The possibility that the threshold for color center formation may be due to the bond straining associated to compaction by irradiation would account for the coincidence between both thresholds and should be investigated in further works. This may reveal the connection between the macroscopic and microscopic effects of irradiation.

In summary, the data offered in this work suggest that electronic excitation plays an important role in the generation of point defects in silica under SHI irradiation. In view of the available theoretical and experimental information, one may safely propose that the color centers are generated by non-radiative decay of self-trapped excitons and that no approximated values for the energetic yield of the electronic processes have been calculated, providing relevant information for scientists and engineers dealing with ion-beam damage to materials.

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