The formation of Ti–O tetrahedra and band gap reduction in SiO$_2$ via pulsed ion implantation

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Titanium ions are implanted into amorphous SiO$_2$ at two different fluences using pulsed ion implantation, and the resulting samples are annealed. Bulk sensitive soft X-ray absorption spectroscopy of the Ti $L_{2,3}$ edge reveal strikingly different spectra for the two fluences. Spectral simulations using multiplet crystal field theory show clearly that for low fluence the Ti ions have a local octahedral coordination, while at higher fluence the formation of Ti$^{4+}$–O tetrahedra dominates. Using O $K$-edge X-ray absorption and emission, the effect of the Ti states on the valence and conduction bands of the host SiO$_2$ is revealed. With the introduction of Ti tetrahedra, the band gap reduces from about 8 eV to just over 4 eV, due entirely to the Ti 3d conduction band states. These results demonstrate the possibility to obtain Ti–O tetrahedra in silica by Ti ion implantation and a suitable thermal treatment, clarify the mechanism of band gap reduction with Ti doping in SiO$_2$, and demonstrate the sensitivity of L-edge X-ray absorption with a multiplet crystal field theory analysis to the Ti coordination of novel materials. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4795262]

I. INTRODUCTION

In recent years, the incorporation of 3d transition metals into semiconductors like ZnO and dielectrics like SiO$_2$ has been the topic of a vast number of studies. Such materials show promise for a variety of technological applications based on the properties induced by the metal atoms. In some cases, the homogenous doping of transition metals into semiconductors leads to bulk ferromagnetic behavior, rendering the resulting material a dilute magnetic semiconductor useful for spintronics$^2$ applications. Alternatively, using ion beam synthesis, the formation of metallic or metal-oxide embedded nanoparticles can be achieved.$^{3,4}$ Dielectrics with embedded nanoparticles exhibit many useful properties such as non-linear optical behavior, superparamagnetism, intense photoluminescence, and altered band structures.$^{5,6}$

The incorporation of Ti ions into SiO$_2$ (SiO$_2$:Ti) is an exciting topic because of the electronic properties of the constituents. The combination of the abundant Ti 3d conduction band states (due to the formally empty 3d shell of Ti$^{4+}$) and the very wide band gap of SiO$_2$ implies a situation for strong electronic structure modification upon doping. Several synthesis techniques have been employed to study SiO$_2$:Ti in the past, including flame hydrolysis,$^7$ the sol-gel method,$^8$-11 chemical reduction,$^{12}$ and ion implantation.$^{13-17}$ For certain Ti concentrations using flame hydrolysis or sol-gel, tetrahedral Ti$^{4+}$ coordination has been found.$^7$-9,11 However, using the ion implantation technique, only indirect evidence using UV absorption has been found for Ti$^4_6$ coordination$^{14}$ so far. Other ion implantation studies revealed metallic Ti (Ref. 15) and Ti-composite nanoclusters.$^{13,16,17}$

The strong electronic structure modifications expected for SiO$_2$:Ti as alluded to above have also been only indirectly studied. A reduced band gap of 4 eV was found using optical absorption$^7$ (compared to the pure SiO$_2$ gap of 8–9 eV). However, the individual valence and conduction bands have yet to be probed in the same experiment to show the mechanism behind this gap reduction. A full understanding of this process could yield a method to tailor the band gap through Ti doping.

In the current work we study the implantation of Ti ions into amorphous, bulk SiO$_2$ using periodically pulsed ion implantation followed by thermal annealing. A combination of soft X-ray absorption (XAS) and X-ray emission spectroscopy (XES) is used to directly study the coordination of the Ti ions and the effects of implantation on the bulk electronic structure. Using Ti $L$-edge XAS and multiplet crystal field theory, we show that low fluences lead to octahedrally coordinated Ti while higher fluence promotes the formation of Ti–O tetrahedra. Oxygen $K$-edge XAS and XES reveal the hybridization of the Ti 3d and O 2$p$ states for the Ti–O tetrahedra and show that the band gap narrowing is almost entirely a consequence of the Ti 3d states lowering the conduction band minimum. Our results demonstrate the utility of $L_{2,3}$ XAS for characterizing the Ti coordination in novel materials, demonstrate necessary parameters for producing Ti–O tetrahedra using ion implantation, and reveal the mechanism behind the band gap reduction in SiO$_2$:Ti.

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II. MATERIALS AND METHODS

The amorphous SiO$_2$ ($a$-SiO$_2$) samples used as targets for this study were 99.9% purity, plane-parallel glass plates measuring 1 $\times$ 1 cm$^2$ with surfaces of optical quality and thicknesses of $\sim$0.7 mm. Samples were irradiated with Ti$^+$ ions using a pulsed source with an ion beam current density of $\sim$2 $-$ 7 mA/cm$^2$, implantation energy of 30 keV, and a pulse duration of 400 $\mu$s. Ion fluences of $1 \times 10^{15}$ cm$^{-2}$ and $5 \times 10^{16}$ cm$^{-2}$ were used for two separate samples. During implantation the sample temperature was kept at 250 $^\circ$C. After implantation the samples were annealed in air at 1000 $^\circ$C for 1 h. A high-purity $a$-SiO$_2$ sample was also left unirradiated for use as a reference material.

An additional reference sample consisting of a TiO$_2$:SiO$_2$ mixture with 8% TiO$_2$ by weight was synthesized via melting 99.9% purity TiO$_2$ and SiO$_2$ in a corundum crucible. This stoichiometry corresponds atomic percentages of 2.0% Ti, 31.3% Si, and 66.7% O, or (Si$_{0.94}$Ti$_{0.06}$)O$_2$. The sample was melted under normal atmosphere at 2000 $^\circ$C for 3 h and then slowly cooled. All samples under study and references were prepared in the Ural Federal University (Yekaterinburg, Russia) using methods developed there.

The depth dependence of the Ti ion concentration was calculated using the SRIM program. Simulations were performed using the same materials and implantation parameters implemented in experiment. The implantation of a total number of $10^9$ ions was simulated in order to obtain an adequately converged profile. Note that SRIM does not consider dynamic changes in the host material during the implantation process, so there is no fluence dependence in the profile shape.

Soft XES were measured using Beamline 8.01 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The beamline uses a Rowland circle type diffraction grating spectrometer with a 90° scattering angle, and the incident radiation is plane-polarized within the horizontal scattering plane. Soft XAS were measured using the spherical grating monochromator (SGM) beamline of the Canadian Light Source (CLS) at the University of Saskatchewan. To ensure the entire implantation region was probed, spectra were collected using the bulk sensitive total fluorescence yield detection scheme, again with horizontal plane-polarized incident radiation. Note that for the $L_{2,3}$ edges of transition metal systems often the fluorescence yield is not a true measure of the XAS since the $3d \to 2p$ decay strengths can vary strongly for different XAS final states. However, for Ti$^{4+}$ the $3s$ fluorescence channel is about as equally strong as the $3d$, significantly suppressing the deviations from XAS.

To analyze the Ti $L_{2,3}$ XAS spectra, multiplet crystal field theory (MCFT) simulations were performed. The simulations include full multiplet effects, as well as crystal field perturbations from neighbouring atoms. The calculated spectra were convolved with Lorentzian and Gaussian lineshapes to account for lifetime and experimental broadening, respectively.

III. RESULTS

Figure 1 shows the simulated concentration profile of Ti implanted in SiO$_2$ using the parameters implemented in our experiment. From the simulation we find a projected range of $R_p = 31.8$ nm with a standard deviation (or straggler) of $\sigma_R = 11.8$ nm. Within the SRIM approach, there is no dependence of the profile shape on fluence, but different fluences will obviously lead to different concentrations. Thus, on the left axis of Figure 1 we give the Ti concentration considering an implantation fluence of $5 \times 10^{16}$ cm$^{-2}$ while the right axis gives the concentration simulated for a fluence of $1 \times 10^{15}$ cm$^{-2}$. The horizontal lines of the figure indicate the maximum Ti concentration ($\eta_{\text{max}}$, determined from the peak of a Gaussian lineshape fit to the profile) and the average Ti concentration ($\eta_{\text{ave}}$). For the higher fluence we find $\eta_{\text{max}} = 19.5$ at. % and $\eta_{\text{ave}} = 6.9$ at. % while for the lower fluence we find values of 0.39% and 0.14%, respectively. Thus, the two fluences give average concentrations above and below the Ti concentration of the SiO$_2$:TiO$_2$ reference sample (2.0 at. %, as described earlier).

Figure 2 shows the experimental Ti $L_{2,3}$ XAS spectra for the implanted and reference samples. These spectra arise from the resonant excitation of Ti 2p electrons into bands of largely 3d character and are consequently very sensitive to the Ti oxidation state and coordination geometry. Immediately evident from Figure 2 is that there are striking differences between the spectra for the implanted samples prepared with different fluences. The spectrum for the higher fluence ($5 \times 10^{16}$ cm$^{-2}$) sample is very similar to that of the SiO$_2$:TiO$_2$ reference sample while the lower fluence ($1 \times 10^{15}$ cm$^{-2}$) sample exhibits different peak intensities and splittings. A spectrum recorded from rutile TiO$_2$ is shown in Figure 2 for reference. The spectrum looks very different from the other spectra, but as we shall show the characteristic lineshape from each sample is due to the local bonding symmetry. The different lineshapes are not due to a changing oxidation state; all samples are 4+. A look at the vastly different multiplet structure of a $d^1$ Ti$^{3+}$ ion confirms this.

Transition metal $L_{2,3}$ XAS spectra of oxides and related materials are generally well understood and are well described by MCFT. For the Ti$^{4+}$ cases shown here, the spectra can be roughly divided into two slightly overlapping...
(and interfering) regions which are split apart by the $2p$ spin orbit coupling: the $L_3$ region below $\sim 461$ eV and the $L_2$ region above this point. Within each of these regions, peaks are split apart generally by local crystal field effects. For TiO$_2$, for example, the $L_2$ and $L_3$ regions are split into roughly two peaks each, which correspond approximately to the $e_g$ levels (at higher energies) and $t_{2g}$ levels (at lower energies), due to the $O_h$ coordination of the Ti ions. Note that there are other minor peaks present due to multiplet effects and that the $e_g$ peaks exhibit a small splitting due partially to symmetry distortion and partially due to long-range effects.$^{23,26}$

Since the multiplet structures of these systems are well-described by MCF, simulations were performed to determine the origin of the differences between the samples. The simulation results are shown in Figure 3, along with the corresponding experimental spectra. First considering the higher fluence case, we see excellent agreement is obtained with a calculation of a Ti$^{4+}$ in tetrahedral ($T_d$) symmetry, using a $10D_q$ value of $-0.90$ eV. This $10D_q$ value is the energy splitting of the $e$ and $t_2$ orbitals induced by bonding with neighboring atoms that distort the Ti 3$d$ atomic orbitals from spherical symmetry. The negative sign indicates a tetrahedral $T_d$ rather than octahedral $O_h$ symmetry. This tetrahedral coordination of the Ti ions indicates they have been incorporated into Si sites of the SiO$_2$, and the spectra show a similar shape to experimental spectra of Ti$^{4+}$ in Ba$_2$TiO$_4$. For the lower fluence case, however, the spectrum is best fit with a field of $O_h$ symmetry (all parameters are shown in Table I). Here, a splitting of $1.75$ eV was used, which is similar in magnitude compared to splittings found for other Ti$^{4+}$ $O_h$ systems such as FeTiO$_3$. However, an additional Gaussian-like broadening is present in the experimental spectrum. To best reproduce the experimental data, an additional value of $0.25$ eV was added to the FWHM of the Gaussian convolved with the simulated spectrum, compared to that of the $T_d$ simulation (the same Lorentzian lifetime broadening was applied in each case). This additional broadening suggests that in this case the Ti ions are possibly located in interstitial regions of the SiO$_2$, where varying crystal field effects at different sites with varying geometries would broaden the spectrum. Finally, we note that the evident splitting of the peak at $459.4$ eV for the $1 \times 10^{15}$ cm$^{-2}$ sample indicates there are some $T_d$-coordinated Ti ions in this sample as well. A subtraction of a $50\%$ fraction of the normalized higher fluence spectrum from the normalized $1 \times 10^{15}$ cm$^{-2}$ spectrum strongly suggests that there are some $T_d$-coordinated Ti ions present in the lower fluence sample.

Figure 4 displays the oxygen $K$-edge XAS and XES for the reference $a$-SiO$_2$ and the Ti-containing samples. Using these spectra, one can investigate the oxygen 2$p$ projected conduction and valence bands, respectively. Focusing on the XES first, we see minimal changes in the shape of the spectra for the various samples shown. As clarified in the inset, the spectra only gradually gain a small amount of spectral weight

![FIG. 2. Titanium $L_{2,3}$-edge X-ray absorption spectra for implanted and reference samples. The spectra have been offset vertically for clarity.](image1)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Symmetry</th>
<th>$10D_q$ (eV)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{4+}$</td>
<td>$O_h$</td>
<td>1.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>$T_d$</td>
<td>$-0.90$</td>
<td>0.65</td>
</tr>
</tbody>
</table>
on the low energy side of the main peak as the Ti content is increased. More significant changes are evident in the XAS, however, as prominent features are introduced in the pre-edge region from 531–535 eV as Ti is added to the samples. Stronger changes in the XAS compared to XES are expected, as the formally empty 3d shell of the Ti$^{4+}$ ions means there are no occupied d states to contribute to the XES whereas there are ample empty states to contribute to the XAS.

The conduction band minimum ($CB_{\text{min}}$) and valence band maximum ($VB_{\text{max}}$) can be extracted from the XAS and XES using the second derivative technique, and from these values the electronic band gap can be estimated. The second derivatives of the SiO$_2$ and SiO$_2$:TiO$_2$ spectra are shown at the bottom of Figure 4. It is found that both samples share a common $VB_{\text{max}}$, marked at point a, whereas the SiO$_2$:TiO$_2$ has a much lower conduction band minimum (point b) than pure SiO$_2$ (point c). Computing the differences between the maxima and minima yields estimated band gaps of 8.0 ± 0.3 eV for SiO$_2$ and 4.1 ± 0.3 eV for SiO$_2$:TiO$_2$. Within experimental error, the $5 \times 10^{16}$ cm$^{-2}$ sample has the same $CB_{\text{min}}$ and $VB_{\text{max}}$ as SiO$_2$:TiO$_2$ but is not shown for clarity. These results agree with an earlier optical study. These results also indicate that this reduction in the band gap is due entirely to changes in the conduction band minimum energy.

IV. DISCUSSION

The Ti L edge results show very different relative amounts of $T_d$ Ti coordination for the two samples. Two possible explanations for this can be considered. First, the $T_d$ coordination may be part of a stable phase of material where a certain ratio of Si and Ti is present. When too little Ti is present, it might not be energetically favorable to form Ti–O tetrahedra, and the Ti remains as interstitials. A second explanation is that with higher fluence, more damage to the host SiO$_2$ occurs during implantation. The higher degree of damage might allow for more incorporation of Ti into $T_d$ sites. A preference to either explanation does not seem evident from the present results, but further experiments could be tailored to study this. Moreover, the specific changes induced by annealing could also be studied in future work since previous studies have found clusters of amorphous silicides and highly conductive metallic Ti layers in non-annealed samples synthesized with only slightly higher fluences than those used here.

The application of L-edge XAS would provide a very useful study of the effects of the annealing process.

The oxygen edge results show the Ti induces a large effect on the SiO$_2$ band gap, reducing it to a range that is almost useful for electronic applications. The edge onset region of the O $K$ XAS is generally very sensitive to transition metal 3d and oxygen 2p hybridization whereas the higher energy features are more sensitive to sp hybridization. The 3d-sensitive region near the edge is often split into two peaks, and the degree of splitting is related to the local crystal field splitting. For TiO$_2$ this splitting is very prominent, as shown in the XAS spectrum in Figure 4 (in the region from 530 to 535 eV). For the SiO$_2$:TiO$_2$ and $5 \times 10^{16}$ cm$^{-2}$ samples, however, this splitting is reduced, in agreement with the weaker $T_d$ crystal field splitting found from the Ti L-edge XAS analysis. As clarified in the right hand inset of Figure 4, the lower fluence sample yields a spectrum very similar to the pure SiO$_2$ reference—both show a small bump at $\sim$531.5 eV (likely due to defect states in the SiO$_2$), the two-peaked Ti structure is not obvious, and there is only a somewhat constant increase in spectral weight for the lower fluence spectrum compared to SiO$_2$. The similarity of these spectra is perhaps not surprising, for a few reasons. First, there are $\sim$50 times fewer Ti atoms in the $1 \times 10^{15}$ cm$^{-2}$ sample compared to the $5 \times 10^{16}$ cm$^{-2}$ sample so the Ti $3d$ character is expected to be very weak. Second, if the Ti atoms in the lower fluence sample are located primarily in interstitial regions as suggested earlier, the covalent interaction between the Ti and O atoms will be reduced, compared to the case where they are located in well defined tetrahedra. Third, the extra broadening that smeared the features of the Ti L-edge XAS for the lower fluence sample would also affect the presence of the two-peaked structure in the O $K$ XAS spectrum of this sample. Thus, the lack of distinct Ti $3d$ features in the 530–535 eV region is reasonable. Finally, we note that while the empty d shell for Ti leads to strong conduction band changes, the fuller d shells for elements like Ni and Cu should lead to useful changes in the valence band properties. By combining Ti implantation with Ni or Cu, one could then tailor both the valence and conduction bands, enabling further control over the band gap.

V. CONCLUSIONS

To conclude, we have studied Ti ion implanted SiO$_2$ samples and reference materials using soft XAS and XES.
The sensitivity of the Ti $L_{2,3}$ XAS to the Ti coordination was demonstrated, and it was shown that octahedral Ti coordination (possibly in interstitial regions) can be obtained by lowering the implantation fluence, while for high fluence the Ti showed tetrahedral coordination. Oxygen $K$-edge XAS spectra were used to probe the hybridization of the Ti $3d$ and O $2p$ states in the conduction band. Strong hybridization was observed for the high fluence and reference samples whereas the low fluence sample showed minimal interaction. From the oxygen XAS and XES the band gaps were extracted, yielding $8.0 \pm 0.3$ eV for SiO$_2$ and $4.1 \pm 0.3$ eV for a sample implanted with $5 \times 10^{16}$ cm$^{-2}$ ions (and for a SiO$_2$:TiO$_2$ reference sample). These results demonstrate a change in Ti coordination with a change in fluence and the same post-implantation annealing, reveal the mechanism behind band gap reduction in SiO$_2$:Ti materials, and show the applicability of $L$-edge XAS with a multiplet crystal field theory interpretation for studying Ti coordination in novel materials.

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