Quantifying inhomogeneities in silicon-rich oxide thin films

Mile Ivanda, Davor Ristić, Giorgo Speranza, and Maurizio Ferrari

Spectroscopic techniques can be used to estimate structural inhomogeneities in silicon oxide thin films.

Nonstoichiometric silicon oxide (SiO$_x$ with $x < 2$) thin films are technologically relevant materials because they serve as thin boundary layers between crystalline silicon and thermally grown oxides in many electronics and optoelectronics. The presence of these boundary oxides strongly affects the electronic properties of silicon.

After detecting visible luminescence in porous silicon, researchers began using an annealing process to produce nanocrystalline silicon from silicon-rich oxides. Producing nanocrystalline silicon from SiO$_x$ thin films offers an advantage because SiO$_x$ thin films can be created using CMOS-compatible methods. The performance and properties of electronic devices and light-emitting materials are dictated by the quality of the silicon-rich oxide films, which is influenced by inhomogeneities in the films. While the real microscopic structure of SiO$_x$ is still a subject of debate, studies have been conducted to establish the composition and structure of SiO$_x$ phases.

Particular attention has been paid to three models that describe the global structure of an SiO$_x$ network: the mixture model, the random bonding model, and the intermediate model. However, the structure of SiO$_x$ and the effective use of one model appears to depend on the specific fabrication technique of the films. For our work, we prepared SiO$_x$ thin films using low-pressure chemical vapor deposition (LPCVD), quantified inhomogeneities in the deposited films using a variety of spectroscopic techniques, drew conclusions about the relationship between the silicon-rich structures and the oxygen content in the films, and evaluated which model best characterized our films.

We prepared SiO$_x$ thin films using LPCVD at 570°C with silane gas diluted with argon and oxygen as the reactant gases. We produced five samples (S1–S5) with varied oxygen contents and confirmed their amorphous structures using Raman spectroscopy. Next, we estimated the oxygen content in the films using time-of-flight elastic recoil detection analysis (TOF-ERDA) and energy-dispersive x-ray spectroscopy (EDX). We also used ellipsometry (for films less than 100nm thick) and m-line measurements (for films greater than 100nm thick) to determine...
the complex refractive index of the deposited films. From the complex refractive indices, we estimated the oxygen content in the films using Bruggeman’s effective medium approximation (EMA). Next, we used IR spectroscopy, which estimates oxygen content from the position \( \omega \) (in cm\(^{-1}\)) of the Si-O stretching mode\(^9\) by:

\[
x = \frac{\omega - 940}{60}
\]

We observed a shift in the position of the Si-O stretching mode peak with increasing oxygen content in our samples: see Figure 1(a). We obtained consistent estimations of oxygen content using TOF-ERDA, EDX, and EMA, but the estimations we acquired using IR spectroscopy for Si1–S4 corresponded to systematically higher oxygen contents: see Figure 1(b). This effect can be explained by the inhomogeneous distribution of oxygen atoms in the films. In IR spectroscopy, the position of the Si-O stretching peak does not depend on the real oxygen content, \( x \), but on the microscopic amount of oxygen atoms around a given silicon atom. Therefore, IR spectroscopy estimates can suffer from non-negligible errors if the oxygen is non-homogeneously distributed in the sample. In particular, if the oxygen atoms in a non-negligible fraction of the matrix form SiO\(_x\) clusters (\( y > x \)), then the oxygen content shown by the IR spectra would be equal to \( y \) rather than \( x \).

Due to the disparate estimation of oxygen content using IR spectroscopy, we concluded that the structure of our films did not correspond to the random bonding model, which describes the SiO\(_x\) structure as a single-phase system consisting of a number of homogenously distributed random bonded Si-(Si\(_{m}O_{n}\)) tetrahedra \((0 < n < 4)\). In the mixture model, a phase separation of the SiO\(_x\) structure into two components—one richer in silicon and the other richer in oxygen—is assumed as:

\[
\text{SiO}_x \rightarrow \frac{x}{y-z}\text{SiO}_y + \frac{y-x}{y-z}\text{SiO}_2,
\]

where the oxygen content in the two separated phases, \( y \) and \( z \), are used as fit parameters. The intermediate model assumes a smooth variation of the chemical composition at the boundaries between silicon clusters and SiO\(_2\) matrix, leading to a continuous variation of the oxygen content.

Next, we further quantified the structural inhomogeneities we detected with IR spectroscopy using x-ray photoelectron spectroscopy (XPS), which is sensitive to the specific chemical bond formed by oxygen with silicon in its different degree of oxidation. We determined \( x \) from the experimental intensities of the different Si 2p core level components using the formula:\(^4\)

\[
x = 0.5 I(Si^{1+}) + I(Si^{2+}) + 1.5 I(Si^{3+}) + 2 I(Si^{4+}).
\]

where the overall intensity of the Si 2p core level was normalized to unity. We fit the spectrum of the Si\(^0\) peak to two Gaussians corresponding to the two spin-orbit Si\(^0\) levels. The other peaks were fit using Gaussian components and by assuming a constant energy shift of the Si\(^{1+}\), Si\(^{2+}\), and Si\(^{3+}\) peaks from the midpoint between the two spin-orbit split components of Si\(^0\) to the Si\(^{4+}\) peak. We used the intensities of the peaks as fitting parameters and varied the position of the Si\(^{4+}\) component and the midpoint between the Si\(^0\) components to optimize the fit. The widths of the peaks and their energy separation were kept constant.

The XPS method yielded a slightly higher value for oxygen content (0.4–0.5 higher) than the TOF-ERDA, EDX, and ellipsometry methods. These results can be explained by surface oxide. The XPS probe depth was approximately 6nm, while the native oxide depth could have been 1–2nm. XPS analysis of the Si 2p core levels confirmed inhomogeneous distribution of oxygen atoms in the films and an almost-complete separation of the silicon-rich oxides into amorphous silicon (\( z = 0 \)) and silicon dioxide (\( y = 2 \)): see Figure 1(c). The fit provided values of \( y > 1.7 \) and \( z < 0.22 \). These results indicated that the mixture model was the most appropriate model for our films.

The quality of silicon-rich oxide films plays a crucial role in electronics and optoelectronics. In this work, we measured inhomogeneities in nonstoichiometric silicon oxide thin films using a variety of analytical techniques. IR absorption spectroscopy estimated higher levels of oxygen than TOF-ERDA, EDX, and ellipsometry and m-line measurements using Bruggeman’s EMA. This finding can be explained by inhomogeneities due to phase separation of the oxygen-rich SiO\(_x\) and silicon-rich SiO\(_2\) (\( y > x > z \)) structures. This phase separation was further quantified using the XPS technique. The XPS spectra of the Si 2p core levels showed an almost-complete phase separation of the SiO\(_x\) films into amorphous silicon and silica. The results indicated that the structure of the samples was best described by the mixture model. Future work will include using the model to develop detailed structural analysis procedures.

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Author Information

Mile Ivanda
Rudjer Boskovic Institute
Zagreb, Croatia

Mile Ivanda is senior researcher and head of the Molecular Physics Laboratory. He develops nanofabrication silicon devices, including silicon-based thin films for sensing and thermoelectric applications.

Davor Ristić and Maurizio Ferrari
Characterization and Development of Materials for Photonics and Optoelectronics (CSMFO) Laboratory
National Research Council-Istituto di Fotonica e Nanotecnologie (CNR-IFN)
Trento, Italy

Giorgo Speranza
Fondazione Bruno Kessler
Trento, Italy

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