Structural properties of annealed SiO\textsubscript{x}

G Nicotra\textsuperscript{1}, C Bongiorno\textsuperscript{1}, M Miritello\textsuperscript{2}, F Priolo\textsuperscript{2} and C Spinella\textsuperscript{1}

\textsuperscript{1}CNR-IMM, Stradale Primosole 50, 95121 Catania, Italy
\textsuperscript{2}MATIS CNR-INFM and Dipartimento di Fisica, Università di Catania, Via S. Sofia 64, 95123 Catania, Italy

E-mail: giuseppe.nicotra@imm.cnr.it

Abstract. On the basis of recent results, concerning the quantitative determination of the clustered silicon concentration in substoichiometric silicon oxide layer and based on electron energy loss spectroscopy (EELS) and energy-filtered transmission electron microscopy, in this paper we demonstrate that the structural properties of Si nanoclusters (Si ncs) strongly depend on the technique used for specimen preparation. In particular here we report on annealed SiO\textsubscript{x} films prepared by plasma enhanced chemical vapour deposition (PECVD) and magnetron sputtering, showing that their structural properties are very different. It is shown that in PECVD films only around 30\% of the Si excess agglomerates in clusters while an almost complete agglomeration occurs in sputtered films. These data are explained on the basis of the different initial structural properties of the as-deposited films which become crucial for the subsequent evolution.

1. Introduction

Silicon oxide films are present in almost all microelectronic and optoelectronic integrated circuits. The synthesis and the precise control of Si nanostructures embedded in a silicon oxide host one important capability, given the possibility of exploiting this system to obtain new functions in novel devices for microelectronics and for optoelectronics [1,8].

There are several techniques to synthesize a Si-rich silicon oxide (SRSO), among them Si ion implantation in silica [2,4], electron-beam deposition [5-6], PECVD [1,8] and magnetron sputtering [7] are the most used. Si nanoclusters (ncs) embedded into a SiO\textsubscript{2} matrix are achieved after thermal annealing thus producing a phase separation between Si and silica. The size distribution properties depend both on the Si excess and on the thermal budget of the subsequent anneal [1]. Energy filtered transmission electron microscopy (EFTEM) studies have shown that clusters start in the amorphous phase and became progressively crystalline only above 1000°C [8]. In spite of the fact that SRSO is obtained by several different techniques, an accurate study defining the similarities and differences among materials produced by different methods is indeed lacking. In this paper we investigate and compare the structural properties of SRSO layers obtained by PECVD and magnetron sputtering. We demonstrate that, in contrast to what is generally believed, properties of films grown by different methods are indeed very different as a result of the agglomeration processes. Implications of these results will be discussed.
2. Experimental
SiO$_x$ thin films (with a total Si concentration in the range 35–55 at.%, corresponding to Si excesses ranging from $1.8 \times 10^{21}$ to $2.8 \times 10^{22}$ at./cm$^3$) have been grown by using a parallel plate PECVD system and an ultra-high vacuum magnetron sputtering system. The substrates have been heated at 300-400 °C during the deposition [1,10]. After deposition, the SiO$_x$ films have been annealed for 1h at temperatures between 1000 and 1300°C in ultra-pure N$_2$ atmosphere. The structural properties of both as-deposited and annealed SiO$_x$ films have been studied by EFTEM carried out in cross-sectional configuration by using a JEOL JEM 2010F TEM/STEM equipped with a 200-kV Schottky field-emission electron gun and an ultra high-resolution objective lens pole piece. The energy filter is a post-column Gatan Image Filter (GIF) with a 1k x 1k CCD. Samples were thinned by mechanical lapping, followed by ion milling using a 4 keV Ar$^+$ beam incident at an angle of 8° and 6° in the final step. Under these conditions the thinning procedure does not induce appreciable extra heating of the sample and consequent modifications of his structure. EFTEM allows to detect Si nc (both crystalline and amorphous and independent of the crystal orientation) dispersed in a SiO$_2$ matrix, due to the different plasmon loss energies in Si and in silica. All the analyses have been performed in regions thin enough to avoid projection effect by the superposition of ncs.

![Figure 1](image1.png)

**Figure 1.** EFTEM images of the SiO$_x$ films at the same Si excess and prepared by PECVD (a) and sputtering (b). Bright zones are associated with the presence of Si ncs. EELS low-loss spectra, open squares, for as-deposited PECVD (c) and sputtered (d) SiO$_x$ films respectively. Continuous lines are the fits to the spectra, performed according to the Barrera-Fuchs model.
3. Result and discussion

Samples have been analyzed by EFTEM. In figure 1 the analyses of a PECVD sample (a), and a sputtered sample (b) both with a Si excess of about $1.6 \times 10^{22}$ at./cm$^3$ and annealed at $1100 \degree$C are shown. It is evident that the Si ncs, appearing as bright regions on a dark background, are much larger in sputtered samples (the mean radius is 4 nm for the sputtered sample and 2 nm for the PECVD one). We have hence performed a quantitative analysis of the EFTEM data, by estimating the amount of Si clustered within the nanostructures.

This task has been performed by using previously established analytical methodologies, based on the measurement of the Si ncs mean size and density [8], or on the analysis of the shape of the electron energy loss spectra [11], based on the Barrera-Fuchs model [12]. From this fitting procedure we find a unique parameter which is the clustered Si volume fraction $f_c$. The values $f_c=11\%$ and $f_c=24\%$ have been obtained in figure 1 (c) for the PECVD sample, and (d) for the sputtered one respectively. This study has been performed on many other samples and the results for both sputtered and PECVD samples having different amounts of Si, all annealed at $1100 \degree$C, are reported in figure 2.

The figure reports the Si present in form of Si nc as a function of the amount of Si excess measured by Rutherford Back-scattering (RBS). In this graph the dashed line denotes complete phase separation between Si and SiO$_2$, while the continuous one is a guide for the eyes. It is clear that in PECVD samples (open circles) only about 30\% of the Si in excess agglomerates while the rest remains dispersed in the matrix. This behaviour had indeed been observed before [8,11,13]. In contrast, sputtered samples (solid circles) show an almost complete agglomeration of the excess Si in ncs, with the matrix remaining as almost stoichiometric SiO$_2$. A question arises on why there is this strong difference in agglomeration properties of the Si ncs in samples prepared by different methods. The presence of N contamination in the former samples coming from the growth method employing N$_2$O as one of the gaseous precursors [1] is not believed to be the main reason, since the presence of Si-N bonds is expected to lead to an easier phase separation with respect to Si-O bonds [14]. In fact, phase
separation and Si ncs formation require the nucleation of Si clusters and their growth through atomic mass transport. It is the starting properties of the as-deposited samples that should be profoundly different and give rise to a different evolution of the two systems. Indeed, the structure of SiO\textsubscript{x} can be described as a simple Si/SiO\textsubscript{2} mixture (random mixture model (RMM) [15]), so proposing phase separation and neglecting the existence of Si intermediate oxidation states, or, alternatively, as a mixture of all Si oxidation states able to respect the overall film stoichiometry (random bonding model (RBM) [16]). In general the two models represent two different extremes and both “pure” models have never been verified. Films can therefore be “more” similar to a RMM or to a RBM and this should affect their thermal evolution. We have hence studied the as-deposited samples by EELS in the electron microscope. Figure 3 reports the EFTEM images and the low-loss EELS spectra for as-deposited PECVD ((a) and (c)) and sputtered ((b) and (d)) SiO\textsubscript{x} films, having the same Si excess of the samples shown in figure 1. The EELS spectra are background subtracted by power law model. It is quite clear that the energy loss of the sputtered sample (d) has a marked component at lower energies, around the bulk Si plasmon (17 eV), whilst the one coming from the PECVD sample (c) is shifted to higher energies, around the bulk SiO\textsubscript{2} plasmon (at 23 eV). It should be emphasized that EFTEM imaging at 17 eV has not evidenced the presence of Si ncs in both samples. However, the circumstance that the energy loss spectrum of the sputtered sample is peaked at 17 eV is a strong indication that the Si-SiO\textsubscript{2} phase separation has already occurred in that as-deposited sample with Si domains whose size is possibly below the detectable limit of the EFTEM imaging technique for the used energies (cluster radii lower than 0.7 nm).

Figure 3. EFTEM images of the as-deposited SiO\textsubscript{x} films having the same Si excess and prepared by PECVD (a) and sputtering (b). EELS low-loss spectra, open squares, for as-deposited PECVD (c) and sputtered (d) SiO\textsubscript{x} films respectively. Continuous lines are the fits to the spectra, performed according to the Barrera-Fuchs model. Both films have the same Si excess as those shown in figure 1.
Then we tried to fit the spectra shown in figure 3 by using the Barrera-Fuchs model [12], i.e. by assuming that the electron energy loss probability, in the plasmonic region (5–30 eV), is given by the sum of three contributions coming from pure SiO$_2$ (the host), pure spherical Si ncs having a well defined size, and surface plasmon losses coming from the Si-SiO$_2$ interfaces, weighted by the unique parameter $f_c$. We imposed a Si nc radius of 0.7 nm consistent with the experimental evidence that the clusters are not visible by EFTEM at 16eV. The best fit to the spectrum coming from the as-deposited samples (continuous line in figure 3 (c,d)) was found for $f_c = 11\%$ and $f_c = 31\%$ of the Si excess, respectively, which is roughly equal to the Si excess present in the film. These values are roughly equal to the fraction of clustered Si detected in the same samples after thermal annealing. Therefore, virtually invisible Si nc are already present in the as-deposited SiO$_x$ layers prepared by both the investigated techniques; these clusters account for almost all the Si excess for sputtered samples, which therefore have a structure closely resembling that predicted by a pure RMM. In contrast a PECVD film presents a structure more similar to the RBM. Small deviations from pure RBM [17] are commonly observed in CVD films [18]; the energy transferred to the incoming atoms by the plasma, and/or the surface mobility due to the substrate heating allow for a partial, chemistry-driven rearrangement of the growing film. The same argument holds also for sputtered films, where the very high energy associated to the sputtered atoms leads to the formation of the most stable phases (Si and SiO$_2$) and therefore to an almost complete phase separation. As a cross check we also investigated the matrix surrounding the Si ncs by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscopy (STEM) configuration. The incident electron beam was focused to a 0.5 nm spot radius and scanned along a straight line connecting two adjacent Si clusters.

![Figure 4](image)

**Figure 4.** EELS core-loss spectra, dashed line, of the matrix surrounding Si ncs taken by STEM in between two adjacent ncs for PECVD (a) and sputtered (b) films. The continuous line in both panels is for pure SiO$_2$.

Dashed lines in figure 4 show the correspondent core-loss spectra of the PECVD (a) and of the sputtered sample (b) taken at a point in between the two examined clusters, i.e., in a region where only the matrix is visible in the micrographs of figure 1. We can observe that the core-loss spectrum taken
in the sputtered sample is identical to the one taken on a reference SiO$_2$ sample (continuous lines in figure 4). This is not true for the spectrum coming from the PECVD sample since it is significantly different from the SiO$_2$ one, thus confirming that in this latter case the matrix is only partially depleted from all the silicon excess initially dispersed in it. In the same time, EELS spectra recorded in the energy region between 99-104 eV, and acquired in the matrix among two adjacent Si clusters in the annealed PECVD sample, exhibit a complex shape indicative of the presence of silicon atoms in their different oxidation states, cf. dashed line of figure 4 (a), which confirms again that PECVD film presents a structure more similar to the RBM. It is clear that the starting properties of the two materials determine the different evolution. EFTEM data suggest also that the thermal evolution of both PECVD and sputtered films does not really imply formation of new clusters, but simply the growth of those already existing in as-deposited films.

4. Conclusion
In conclusion, we have demonstrated that the structural properties of SRSO films strongly depend on the deposition method. In particular, while at lower annealing temperatures samples deposited by sputtering present an almost full agglomeration of the Si excess atoms, films grown by PECVD present agglomeration of only a small fraction of the Si excess. These data are explained on the basis of the different structures of the as deposited films.

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