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# Deposition on thin $SiO_2$ layer by reactive sputtering

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We investigate the experimental possibilities for producing high purity stoichiometric $SiO_2$ thin films by reactive ion beam sputtering. The layers were deposited in a UHV chamber (base pressure $4\times10^{-9}$ mbar) by 1 keV $Ar^+$ ions for sputtering from a high purity silicon target, using different values of the oxygen partial pressure ($5\times10^{-6}$ - $1\times10^{-3}$ mbar) and of the ion beam current on the target (1.67 - 6.85 mA). The argon partial pressure during ion gun operation was $1\times10^{-3}$ mbar. The substrates were held at room temperature or at 550 °C, and the films were deposited to 12.5 - 150 nm, at a rate from 0.0018 - 0.035 nm/s. To perform structural characterization we used Rutherford backscattering spectrometry, electron microprobe, X-ray diffraction and Raman spectroscopy. From the results it is clear that reactive ion beam sputtering proved to be efficient for deposition of high quality silica films at 550 ºC, oxygen partial pressure of $2\times10^{-4}$ mbar (ion beam current on the target from 5 to 5.5 mA) or at a lower deposition rate, ion beam current of 1.67 mA and oxygen partial pressure of $6\times10^{-5}$ mbar. The aim of these investigations was also to study the consumption of oxygen from the gas cylinder. We found that it is lower for higher deposition rates.

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## 1. Introduction

Two important aspects are currently related to silicon-dioxide. It is well known that $SiO_2$ is one of the most important materials in the field of microelectronics. On the other hand, $SiO_2$ is the basic material for the understanding of the behaviour of oxide glasses, used for nuclear waste storage. A critical point in both cases is diffusion of components. It was observed, for example, that silicon diffuses in an oxide film during thermal growth of $SiO_2$ on silicon substrates [1-8]. As for the nuclear glasses, they are exposed to irradiation, which can influence many physical processes, one of the most important being self-diffusion [9]. To develop a new generation of materials (nanoelectronics, nuclear glasses), a detailed understanding of the diffusion processes is essential.

To study diffusion mechanisms and determine a general model for ageing of nuclear glasses, we need stoichiometric $SiO_2$ thin films. Roma *et al* [10] have reported the first theoretical results for oxygen self-diffusion in $SiO_2$. They have considered two distinct modes – the *closed mode*, when no exchange is possible with the atmosphere, and the *open mode*, when exchange with the atmosphere is allowed. In order to verify their results, special techniques are needed to prepare the $SiO_2$ samples. Quantitative measurements of oxygen self-diffusion in $SiO_2$ is feasible in $Si(^{18}O)_2/Si(^{16}O)_2$ bilayer structures using secondary ion mass spectrometry (SIMS), which can clearly distinguish between these two isotopes. In this context, reactive ion beam sputtering offers advantage such as precise control of oxygen partial pressure during the deposition process.

The aim of this article is to determine the experimental conditions for producing high purity stoichiometric $SiO_2$ thin films. We have applied the reactive ion beam sputtering technique from a pure Si target, for two obvious reasons: (i) it provides a good control of deposition parameters and of the layer thickness; and (ii) an rf sputtering technique would not be possible for deposition of $Si(^{18}O)_2$ films, as such targets are not available. All experiments in this study were performed with $(^{16}O)_2$, because the use of $(^{18}O)_2$ would be too costly for these purposes. It was found that high quality stoichiometric $SiO_2$ thin films can be produced by a suitable adjustment of deposition parameters.

## 2. Experimental methods

The layers were deposited by reactive ion beam sputtering in a UHV chamber. The base pressure in the deposition chamber was $4\times10^{-9}$ mbar. We have used a high purity silicon target (diameter 76 mm), which was bombarded with 1 keV $Ar^+$ ions, at 45° incidence angle. The ion source was an ERIS type ion gun (Electrostatic Reflex Ion Source), irradiating about 1 $cm^2$ area of the target. The ion beam current on the target, $I_t$, was varied from 1.67 to 6.85 mA, using a constant argon (purity 99.996%) partial pressure of $1\times10^{-3}$ mbar. We have applied different values of the oxygen (purity 99.995%) partial pressure $P_O$, from $5\times10^{-6}$ to $1\times10^{-3}$ mbar for reactive deposition. In these experiments we used $(^{16}O)_2$ and the substrates of quasi-monocrystalline graphite (10 mm × 10 mm), silicon (15 mm × 8 mm), silica glass (20 mm × 40 mm) and $B_4C$ (diameter 15 mm). Before deposition, the substrates were cleaned by standard chemical procedures. They were placed parallel to the target, at a distance of 150 mm. During deposition the substrates were held at room temperature or at 550°C. The $SiO_x$ films were deposited at

a rate from 0.0018 - 0.035 nm/s to a thickness of 12.5 - 150 nm.

The thickness of the films was determined by a surface profilometer on the optically flat silicon substrates. Structural characterization of the films was performed by Rutherford backscattering spectrometry (RBS), electron microprobe, X-ray diffraction (XRD) and Raman spectroscopy. For RBS analysis we used a 1 MeV $He^+$ ion beam at normal incidence and the detector at 165° backscattering angle. Experimental spectra were analysed with the programme PERM, version 2003.02 [11,12]. Electron microprobe analysis was done in the wavelength dispersion mode, with the electron microprobe CAMECA SX 50. XRD analysis has been done using a BRUKER D8 Advance X-ray diffractometer. We used parallel beam geometry with Göbel mirror, and $C_u$ $K_\alpha$ X-rays in the 2θ range from 5° to 32°. Incident angle of the Göbel mirror was 3°, step was 0.05° and time was 50 s per step. For Raman analysis we used a Jobin Yvon model U-1000 monochromator, with a conventional photocounting system. The room temperature Raman spectrum was excited by the 488 nm and 514.5 nm lines of an argon laser (the average power was about 50 mW) in the backscattering geometry.

## 3. Results and discussion

First depositions were made at room temperature. RBS analysis of a $SiO_x/B_4C$ sample, deposited at room temperature, $P_O = 1\times10^{-3}$ mbar and $I_t = 6.85$ mA, indicated an over-stoichiometry of oxygen ($SiO_{2.3}$) and argon incorporation. Thermal annealing (1000 °C, 27 hours) nicely improved the stoichiometry but failed to eliminate the argon incorporation. In order to avoid incorporation of argon, in further experiments we heated the substrate-holder to 550 °C.

RBS analysis of a $SiO_x$/glass sample, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t = 5$ mA, is shown in Fig. 1. The experimental spectrum shows surface signals from silicon and oxygen, but it can be seen that these signals are overlapped by the signals arising from the substrate. As the glass substrate contains known fractions of Na, Mg, Al, K, Ca and Ba, we introduced these elements in the PERM code. This enabled a good agreement between the experimental data and the fitted spectrum. In Fig. 1 we have also shown the separated spectra corresponding to Si, O and the substrate elements in the fit. The extracted depth profiles (not shown) indicate that we reached the $SiO_2$ stoichiometry within RBS incertitude. Also, deposition at high temperature permitted us to avoid the argon incorporation. However, there is some sodium depletion near the surface of the glass and the sodium signal overlaps the silicon signal. This is not favourable to a sensitive measurement of stoichiometry in the deposited layer.

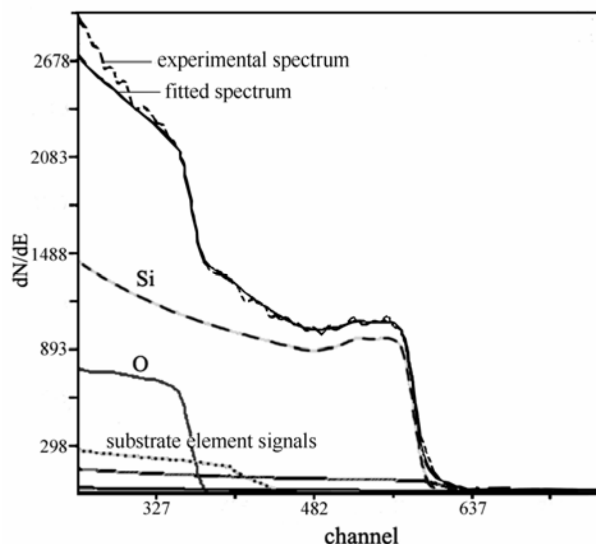


*Fig. 1. RBS analysis (experimental and fitted spectra) of a $SiO_x$/ glass sample, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t = 5$ mA.*

In order to confirm the layer stoichiometry, we used the substrate of quasi-monocrystalline graphite. The RBS analysis of a $SiO_x$/graphite sample, deposited under the same conditions as the previous sample but with a slightly higher $I_t$ (5.5 mA), is shown in Fig. 2. Here the signals from Si and O are well separated from the graphite substrate, which provided a more reliable determination of these profiles. Indeed, a good fit with the experimental data (Fig. 2a) could be obtained by introducing only Si, O and C in the PERM code. Fig. 2b shows the extracted concentration profiles, from where we can see the $SiO_2$ stoichiometry of the deposited layer within RBS incertitude. A slight drop of oxygen concentration near the surface is due to a premature shut-down of the oxygen inlet. The calculated layer thickness, using bulk density of $SiO_2$, agrees with the value of 125 nm, as measured with the profilometer. This suggests a reasonable purity of the deposited layer.

We could also reach the $SiO_2$ stoichiometry of the layers by using much different deposition parameters than above, i.e. $P_O = 6\times10^{-5}$ mbar and $I_t = 1.67$ mA. The extracted depth profiles of the RBS analysis (experimental and fitted spectra not shown) of a sample produced for these parameters (presented in Fig. 3) indicate a very uniform $SiO_2$ stoichiometry of the deposited layer. However, as the applied $Ar^+$ ion beam current on the target was lower, we had a much lower deposition rate and a small thickness of the layer (12.5 nm).

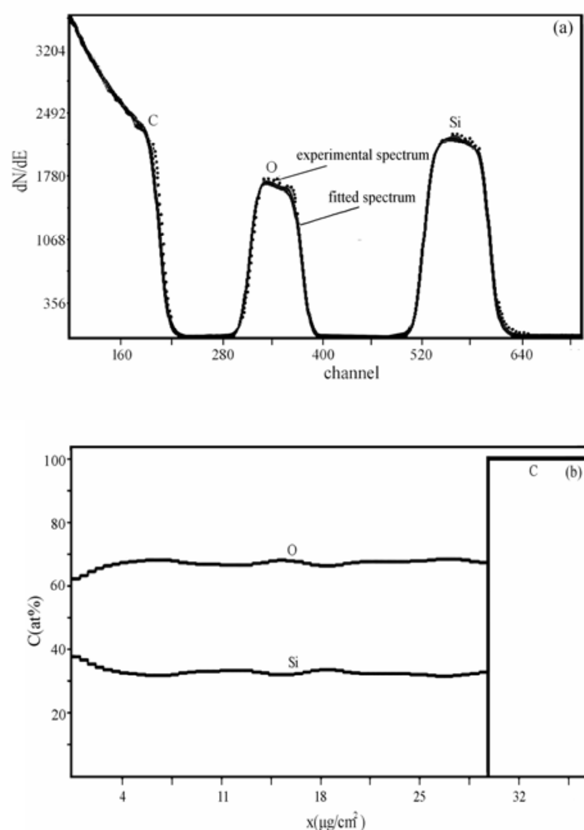


*Fig. 2. RBS analysis of a $SiO_x$/graphite sample, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t = 5.5$ mA: (a) experimental and fitted spectra, and (b) extracted concentration profiles.*

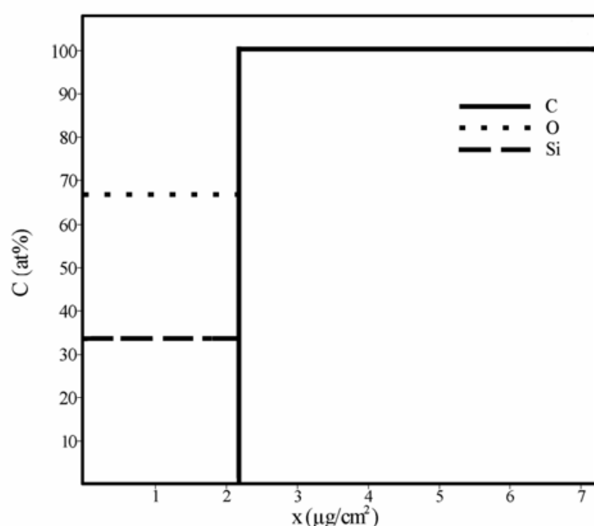


*Fig. 3. Extracted concentration profiles of the RBS analysis of a $SiO_x$/graphite sample, deposited at 550 °C, $P_O = 6\times10^{-5}$ mbar and $I_t = 1.67$ mA.*

One aspect of these investigations was the precise control of the oxygen consumption from the cylinder. For this reason we have applied a constant $I_t$ = 5 mA, at a reduced $P_O$ of $5\times10^{-6}$ mbar, $2\times10^{-5}$ mbar, $5\times10^{-5}$ mbar and $1\times10^{-4}$ mbar. However, RBS analysis gave an under-stoichiometry of oxygen: $SiO_{0.25}$, $SiO_{0.35}$, $SiO_{0.6}$ and $SiO_{1.25}$ respectively. We also tried to use a higher $I_t$ of 6.85 mA, keeping $P_O$ at $2\times10^{-4}$ mbar, but again we observed an under-stoichiometry resulting in $SiO_{1.85}$.

Therefore, we can obtain stoichiometric $SiO_2$ thin films for $P_O = 2\times10^{-4}$ mbar and $I_t$ from 5 to 5.5 mA (deposition rate ~ 0.029 nm/s), or $P_O = 6\times10^{-5}$ mbar and $I_t$ = 1.67 mA (deposition rate 0.0018 nm/s). The advantage of deposition for $P_O = 2\times10^{-4}$ mbar is a much higher deposition rate. The advantage of deposition for $P_O = 6 \times 10^{-5}$ mbar is in a better stability of the ion gun current.

The oxygen consumption during deposition depends on two parameters for a given deposit thickness: the oxygen partial pressure and the ion beam current on the target. Lowering $P_O$, at a given $I_t$, reduces gas consumption. Increasing $I_t$, hence the deposition rate, at a given $P_O$, also reduces the consumption.

To calculate the oxygen consumption in cases of the high and low deposition rates, we measured the pressure loss in the used $(^{16}O)_2$ cylinder, for one hour and calculated the maximal thickness of the layers that can be obtained by using the whole available amount of oxygen. The results show that, with the available quantity of oxygen, we can obtain 2100 nm of a $SiO_2$ thin film for $P_O = 2\times10^{-4}$ mbar and $I_t$ = 5.5 mA, while for $P_O = 6\times10^{-5}$ mbar and $I_t$ = 1.67 mA we would obtain only 400 nm of $SiO_2$. This infers that working with a higher $I_t$ and a higher $P_O$ results in lower oxygen consumption.

Apart from RBS analysis we performed other structural characterization of 125 nm $SiO_2$ films on graphite, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t$ = 5.5 mA. The result of electron microprobe analysis of such a sample is shown in Fig. 4. This analysis shows one silicon $K_\alpha$ line and one oxygen $K_\alpha$ line arising from the layer, confirming the purity of deposited $SiO_2$ thin film.

XRD analysis of the same sample is shown in Fig. 5. The crystalline peaks of $SiO_2$ were not observed. Only a broad diffraction maximum (2θ = 10.5°) can be seen, which indicates an amorphous structure. There is also a narrow (002) crystalline peak of graphite (2θ = 26.45°) which is convoluted with a broad diffraction maximum. This may be due to the presence of microscopic disoriented fragments of graphite produced when cleaving the substrate. It is also possible that some amorphisation by the impinging Si atomic species occurs during the first phase of the layer deposition.

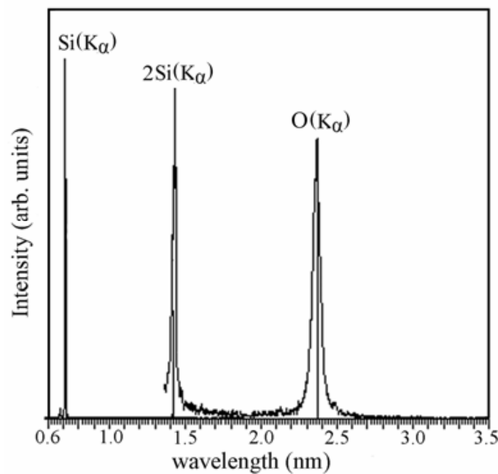


*Fig. 4. Electron microprobe analysis of $SiO_2$/graphite sample, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t = 5.5$ mA.*

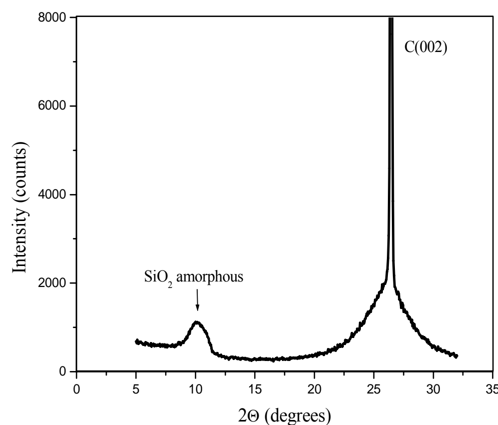


*Fig. 5. XRD analysis of $SiO_2$/graphite sample, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t = 5.5$ mA.*

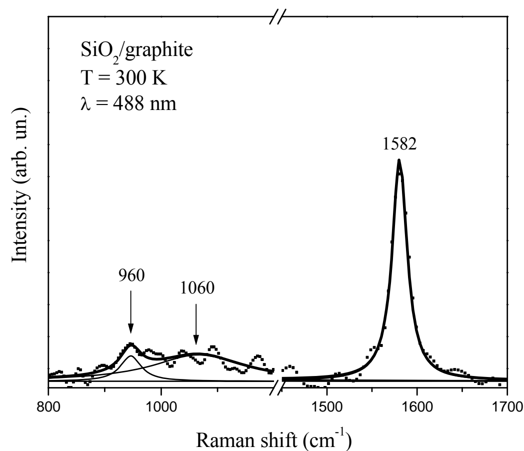


*Fig. 6. Raman spectrum of $SiO_2$/graphite sample, deposited at 550 °C, $P_O = 2\times10^{-4}$ mbar and $I_t = 5.5$ mA.*

The unpolarized Raman spectrum, in the spectral range from 800 $cm^{-1}$ to 1700 $cm^{-1}$, at room temperature, is given in Fig. 6. Experimental results are indicated by small squares. The obtained spectrum was analyzed using the deconvolution technique. All lines are Lorentz type lines [13], which is typical for an amorphous structure. Beside a narrow 1582 $cm^{-1}$ peak, which corresponds to $E_{2g2}$ mode of the graphite [14], in the spectral range from 960 $cm^{-1}$ to 1060 $cm^{-1}$ one can see the lines which indicate $SiO_2$ amorphous structure [15].

## 4. Conclusions

We have shown that the reactive ion beam sputtering technique has proved efficient for deposition of high quality silica films at 550 °C, using an oxygen partial pressure of $2\times10^{-4}$ mbar and ion beam current on the target from 5 to 5.5 mA, or at a lower deposition rate, using ion beam current on the target of 1.67 mA and oxygen partial pressure of $6\cdot10^{-5}$ mbar. We calculated that the oxygen consumption was smaller under $2\times10^{-4}$ mbar partial pressure and the higher ion beam current on the target. The experimental method enables us to control precisely the oxygen consumption during the deposition process. RBS, electron microbe, XRD and Raman analyses have shown that the obtained $SiO_2$ thin films were stoichiometric.

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