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Optical models for ellipsometric characterization of high temperature annealed nanostructured SiO_2 films♣

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Silicon oxide films, vacuum evaporated and annealed in Ar atmosphere at temperatures of 1000 and 1100ºC have been studied by spectroscopic ellipsometry. By the Bruggeman effective-medium approximation, different optical models have been applied for characterization of the nanostructured SiO_x films. The results showed that during annealing at 1000°C, Si clusters were formed in the sub-stoichiometric $SiO_{1.61}$ matrix, which crystallized in nanocrystallites with a volume fraction of ~ 14 %. Annealing at 1100°C transformed the oxide structure to stoichiometric SiO_2 and created 22% nanocrystalline Si inclusions. A silicon dioxide top layer existed in all films, the thickness of which varied with the technological steps and was well correlated with the surface roughness obtained from the AFM imaging.

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1. Introduction

Composites which contain silicon nanocrystals (nc-Si) in SiO_2 or a SiO_x matrix have drawn the attention of many researchers as possible materials for light-emitting silicon-based structures. In the case of thermal annealing of non-stoichiometric silicon oxides, the prime attention has been paid to the observation and characterization of nanometer-sized Si clusters formed in the oxide matrix during this process. The annealing temperature determines the structure of the inclusions, as at temperatures higher than 900°C the amorphous silicon inclusions crystallize, producing nanocrystalline Si (nc-Si) clusters embedded in the amorphous oxide matrix [1-6].

Spectroscopic ellipsometry (SE) is a powerful non-destructive tool for the detection of thermally stimulated changes in the oxide structure and composition, and it gives important additional information about the formation of nano-sized Si inclusions. Multiple angle measurements provide a large number of experimental data, which ensures the accuracy in finding the proper structural model to describe the real structure. The optical constants of the films are computed by fitting the SE measurement data with an appropriate model. The most frequently used models are the Tauc-Lorentz model [7] and those based on the Bruggeman effective medium approximation (BEMA) [7-10].

In this work, we have applied spectroscopic ellipsometry to study SiO_x films deposited by thermal evaporation in a vacuum. In order to stimulate the formation of nc-Si clusters in the oxide matrix, high-temperature annealing has been performed. The films' structure was modelled by applying the BEMA theory. The complex refractive index values were found, and the complex dielectric functions were analysed. Additional information has been gained from atomic-force microscopic (AFM) measurements.

2. Experimental details

Silicon monoxide powder (Cerac Inc., purity of 99.9%) was evaporated to 172 and 425 nm thicknesses, at a residual pressure of ~10^{-3} Pa on crystalline Si (c-Si) substrates kept at 150ºC. The films were thermally annealed in an Ar atmosphere at 1000 and 1100°C for 30 and 15 min, respectively, to generate nc-Si clusters in the oxide.

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Ellipsometric measurements were carried out after each technological step with a "Rudolf Research" manual variable-angle ellipsometer, in the wavelength region 280-820 nm and at different angles of incidence varying from 50^o to 75^o. The thickness, complex refractive index and composition of the films were evaluated from the ellipsometric angles' ψ and Δ data. In the ellipsometric modelling with BEMA theory, the films are considered as a physical mixture of known components: fine-grain polycrystalline-Si (poly-Si), crystalline Si (c-Si), amorphous SiO, amorphous SiO_2 and voids. The dielectric functions of the components were taken from the literature [11-13]. The evaluation software allows one to search simultaneously for the thicknesses of the layers and their compositions. An iterative least-squares method was used for minimizing the difference (mean square error) between the experimental Ψ and Δ data and the theoretical ones.

In addition, AFM measurements were made to support the validity of the ellipsometric models. The surface morphology of the films was studied by recording AFM images on an NT-MDT (Russia) Solver scanning probe microscope. The surface scanning was performed in a semi-contact mode, to avoid altering the sample in subtle ways. Cantilevers with typical force constants of 5.5 N/m, curvature radii of 10 nm and resonant frequencies of 130 kHz were used.

3. Results and discussion

In the optical models, a multi-layer structure was considered, assuming that the film consisted of several sublayers, each having different optical constants and compositions. The composition of the layers was considered as a physical mixture of SiO as a remainder composite, plus SiO_2 and Si as products of the SiO decomposition. Including fine-grain poly-Si as the Si component resulted in better fitting to the experimental data. The actual surface roughness was included in the last top-layer, with a composition of SiO, SiO_2 and 50 % voids. Results from the single-layer model calculations are not included here, but are published elsewhere [6]. The thicknesses and volume fractions of the components were varied until they reached the best fit, showing satisfactory agreement between the experimental and theoretical spectra. The optical model with two sublayers was satisfactory, as introduction of an additional third sub-layer did not improve the fit quality. The models which described best the real structure of the annealed films, gave a minimum mean square error MSE of < 10.

The analysis of the ellipsometric data with a two-layer model revealed that the as-deposited films are not silicon monoxide but SiO_x, with a stoichiometric index x equal to 1.2. A top layer with ~ 3.2 nm thickness and a composition close to stoichiometric silicon oxide was registered.

By annealing at 1000^oC for 30 min, the stoichiometric index increased to x=1.61, as the films still remained a silicon suboxide of $SiO_{1.61}$ with a 13 nm thick top layer being fully oxidized. In the 151 nm thick main layer, 14.2 % of Si crystallites were formed. This is in good agreement with our microscopic observations [6], where the TEM micrographs visualised the nano-sized Si crystallites in the oxide matrix, revealing an average crystallite size of ~ 3 nm. As is evident from Fig. 1, the generated Ψ and Δ spectra, using a two-layer model, fit well to the experimental data.

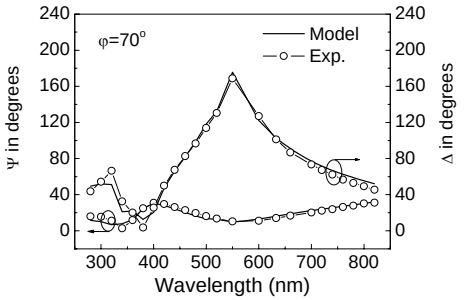
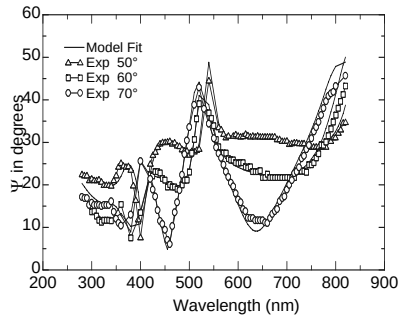


Fig. 1. Experimental (Exp.) and generated (Model) ψ and Δ data as a function of wavelength measured at 70^o on a 164 nm thick film, annealed at 1000^oC.

Annealing at 1100^oC for 15 min resulted in an oxide structure typical of stoichiometric SiO_2 [14], and in an increased volume fraction of Si crystallites of up to 22.3 %. The results of the best fitting procedure, made with the proper model simultaneously for three angles of incidence, are given in Fig. 2. A satisfactory agreement between the experimental data and those generated on the basis of the given model is achieved, the MSE error being 8.1.

The dielectric functions ε $(\varepsilon=\varepsilon_1-i\varepsilon_2)$ obtained through the optical modelling, the real ε_1 and imaginary ε_2, of the as-deposited and annealed films are presented in Figs. 3a and 3b, respectively.

After annealing, the refractive index, and correspondingly ε_1, of the films increased, which



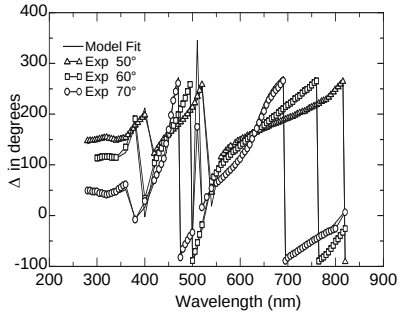


Fig. 2. Experimental (Exp.) and generated (Model) ψ and Δ data as a function of wavelength measured at different angles of incidence on a 391 nm thick film, annealed at 1100°C.

was accompanied with a 5-8 % reduction of the film thickness. This is evidence of the densification of the films during annealing. Formation of nc-Si clusters in the high-temperature annealed films is reflected in an enhancement of the absorption, and correspondingly ε_2, and the appearance of a peculiarity in the ε_2 spectra (Fig. 3) at around 3.4 eV, where the characteristic peak for single crystalline silicon is situated [12]. At 1100°C, ε_2 is not zero, due to the nc-Si inclusions giving a contribution to the absorption.

The surface of the as-deposited films was fairly smooth (Fig. 4). The cross section, made along the y-axis, indicates uniformly distributed hillocks.

High-temperature annealing led to the appearance of randomly distributed hillocks on the smooth surface (Figs. 5 and 6). Their heights became larger, resulting in a larger average roughness of ~14 nm on a 3x3 μm^2 area (Table 1).

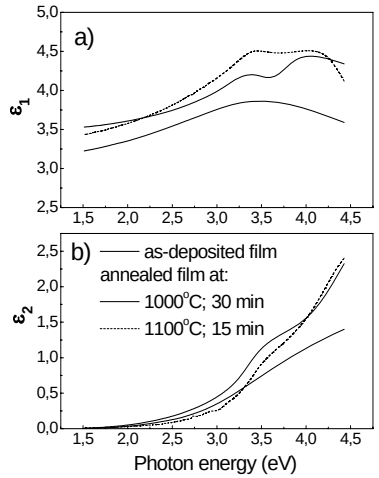


Fig. 3. Dispersion curves ε_1(a) and ε_2 (b) for SiO_x films, before and after annealing.

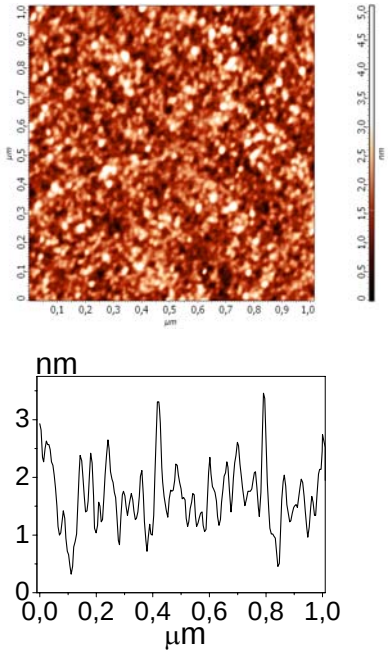


Fig. 4. 2D AFM image (1x1 μm^2) and Y-cross section of an as-deposited SiO_x film.

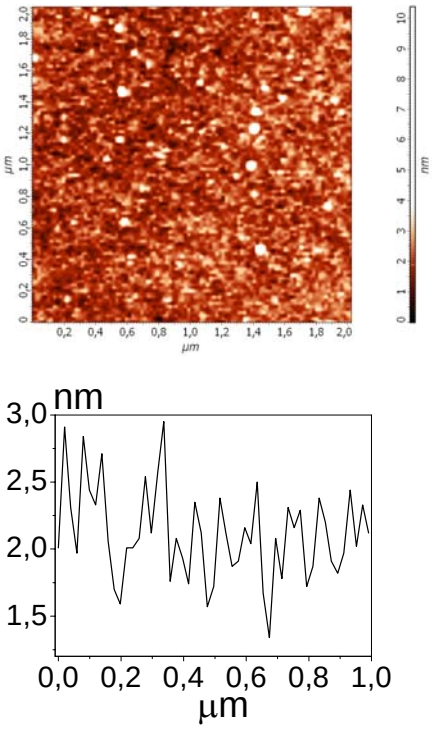


Fig. 5. 2D AFM image (2x2 μm^2) and Y-cross section of a SiO_x film annealed at 1000°C.

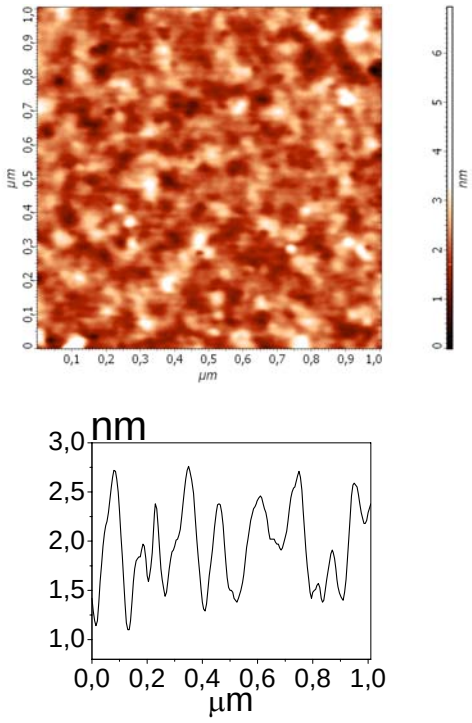


Fig. 6. 2D AFM image (1x1 μm²) and Y-cross section of a SiO_x film annealed at 1100°C.

The observed changes in the surface morphology caused by annealing can be connected to the existence of Si-O phase reconstructions, which proceed upon heat treatment and lead to the formation of SiO_2 and Si inclusions. The latter could be a precursor for the observed hillocks that emerged from the surface due to an accelerated oxidation rate for these Si inclusions. They most probably entirely oxidize to SiO_2 in the surface region, due to the high temperature. This suggestion is supported by the ellipsometric results, which detected a thin stoichiometric SiO_2 layer on the main oxide layer.

The statistical parameters, such as the average roughness S_a; root mean square roughness S_q and peak-to peak deviation S_y are summarized in Table 1. The thickness of the sublayers (main and top layer) calculated from the SE data by applying the two-layer optical model is also included.

Table 1. Average roughness S_a; root mean square roughness S_q and peak-to peak deviation S_y values, taken from a 3x3 μm² area, for series S: A - as-deposited and annealed at 1000°C - B and 1100°C - C . The thickness of the sublayers, obtained from SE data analysis, is also presented.

S	S_a (nm)	S_q (nm)	S_y (nm)	Main layer (nm)	Top layer (nm)
A	0.216	2.107	3.268	169.10	3.2
B	1.496	2.107	13.53	150.95	13.04
C	0,514	0,696	14.36	376.68	14.24

The peak-to-peak deviation in a 3x3 μm² scanning area is well correlated with the thickness of the top-layer of the films, as determined from the optical modelling. These results confirmed the validity of the models applied to the studied films.

4. Conclusions

Silicon oxide films, vacuum evaporated and annealed at temperatures of 1000 and 1100°C, have been studied by spectroscopic ellipsometry. Two-layer optical models well described the films' structure, revealing a $SiO_{1.2}$ suboxide of the as-deposited state. After annealing, Si clusters appeared in the crystalline phase in the $SiO_{1.61}$ and SiO_2 oxide matrices, respectively, with a tendency to increase in volume fraction with increasing temperature. The second top-layer was SiO_2, and its thickness was correlated with the surface roughness, as determined by AFM imaging. The AFM results confirmed the suitability of two-layer optical models, and showed a homogeneous surface morphology and a smooth surface.

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