Journal of Optoelectronics and Advanced Materials, Vol. 7, No. 3, June 2005, p. 1383 - 1387

SILICON CLUSTERS IN SILICON MONOXIDE FILMS

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In this paper, results of ellipsometric, XRD and TEM studies on evaporated and thermally annealed thin SiO_x films are presented. The thickness of the films was determined from the ellipsometric measurements and checked by TEM pictures taken in cross-section mode. The composition of the SiO_x films was estimated by applying different models to simulate the ellipsometric data. It has been shown that annealing at 700 ^oC leads to appearance of amorphous Si clusters. The Si nanoclusters in crystalline phase were found only after annealing at 1000 ^oC. By X-ray scattering measurements, only one crystalline peak is detected, mirroring the (100) orientation of the Si substrate, which suggests that the size of Si nanocrystallites is too small to be observed with XRD, or their volume fraction is too low. The TEM images have proven the presence of crystallized Si clusters in the oxide matrix being randomly distributed and sized between 1 - 4 nm. The ellipsometric modeling results are in good agreement with the XRD and TEM observations, as they detect crystalline Si inclusions at 1000 ^oC with a volume fraction less than 12 %.

(Received April 13, 2005; accepted May 26, 2005)

Keywords: Silicon monoxide, Nanocrystalline Si clusters, Spectral ellipsometry, X-ray diffractometry, Transmission electron microscopy

1. Introduction

Amorphous SiO_x material is very interesting in respect to presence of large number of Si-Si bonds, which are sequently ordered and, hence, can be considered by nature as Si clusters in SiO_X matrix. These small natural Si clusters in SiO_x films can be transformed to nanocrystals under high temperature annealing [1,2]. The defect centers of these Si nanocrystalline clusters in the amorphous oxide matrix are supposed to play an important role in the light emission mechanisms. Appearance of photoluminescence (PL) bands related to the formation of Si nanocrystallites in annealed SiO_x films has been recently reported [3,4]. The photoluminescence efficiency in the visible spectral range is strongly dependent on the size and density of nanocrystalline Si (nc-Si) inclusions [4-6]. Therefore, the control of nc-Si size and density and the chemical composition of the oxide matrix are of great importance for the application of such films in light emitting Si-based devices.

In this paper, results of X-ray diffraction (XRD), transmission electron microscopy (TEM) and spectral ellipsometry (SE) studies on evaporated and thermally annealed thin SiO_x films are presented. The influence of annealing conditions on the composition and structural-phase transformations of the silicon oxides are considered. A good agreement between the results of these measurement methods is established.

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2. Experimental details

Silicon monoxide thin films were deposited onto two-sided polished (100) Si substrates by thermal evaporation of SiO (Cerac Inc., purity of 99.9%) in vacuum at a residual pressure of $2x10^{-3}$ Pa. The substrates were kept at 150^oC during deposition. The films underwent thermal annealing in Ar atmosphere at 700^oC and 1000^oC for 5 or 30 min.

Preliminary information about crystalline phases in the annealed films was obtained applying X-ray diffractometry using Philips X'Pert equipment. The crystalline phases were identified using data of ASTM system [7]. Direct evidence for the formation of nc-Si clusters was obtained from the TEM observations carried out on cross-sectioned samples in a JEOL, JEM 30 electron microscope operating at 300 kV. The cross-sectioned samples were prepared by ion thinning after mechanical polishing.

The film composition was evaluated from the ellipsometric data of measurements performed on a 436 Rudolph ellipsometer in the spectral range of 280-820 nm and at an angle of incidence of 70^o. The spectral dependence of the complex refractive index is considered in detail elsewhere [8] and is not discussed here. The film structure was considered as a mixture of amorphous Si (a-Si), crystalline Si (c-Si), amorphous SiO and amorphous SiO_2 composites, including some voids fraction. The dielectric functions of the composites were taken as references from the literature [9]. Previous study [1] has established that these SiO_x samples possess smooth surfaces and, therefore, no surface roughness was included in the optical models.

3. Results and discussion

Before and after annealing the samples were measured in a large angle range of X-ray scattering (10^o - 100^o) with very small step of 0.001 ^{o}/sec. In Fig. 1 the characteristic X-ray patterns are shown for as-deposited and annealed films. As is seen, the spectra exhibit only one crystalline peak. This peak corresponds to the (004) reflection of the Si single crystal, mirroring the (100) orientation of the Si substrate. In spite of the good resolution of XRD measurements, in the spectra no other crystalline peaks were detected even after prolonged annealing of the SiO_x films at 1000^oC. Therefore, it can be concluded that both, the as-deposited and annealed SiO_x films are XRD-amorphous, which means that if there is Si crystalline phase at all, the size of the nanocrystallites is too small to be observed with this technique, or their density is too low.

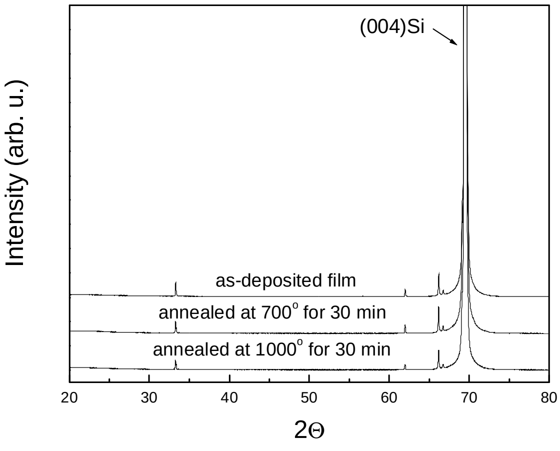
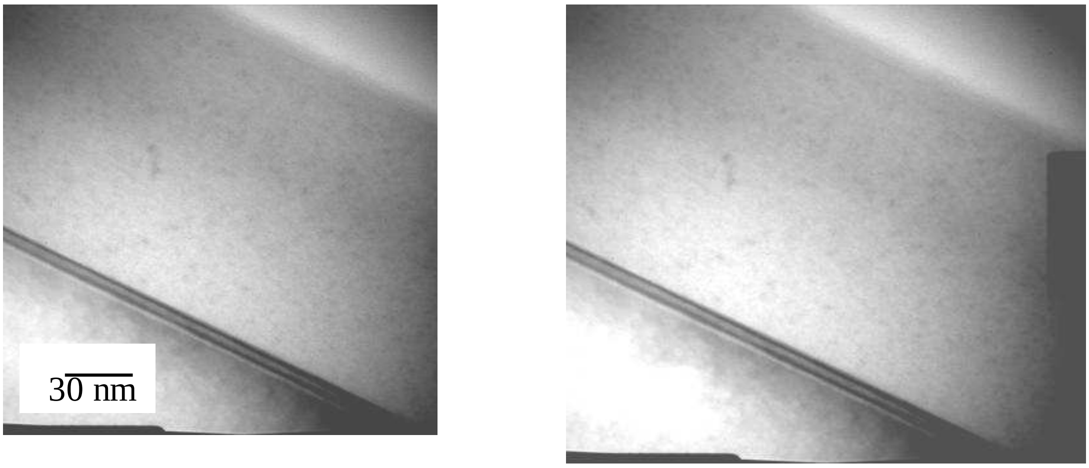


Fig. 1. XRD spectra of SiO_x films measured before and after annealing at 700 and 1000 ^oC for 30 min.

The examinations of the TEM images show clearly that the films have an amorphous structure after annealing at 700^oC, while crystalline phase of Si inclusions appear in the amorphous oxide matrix after annealing at 1000^oC.

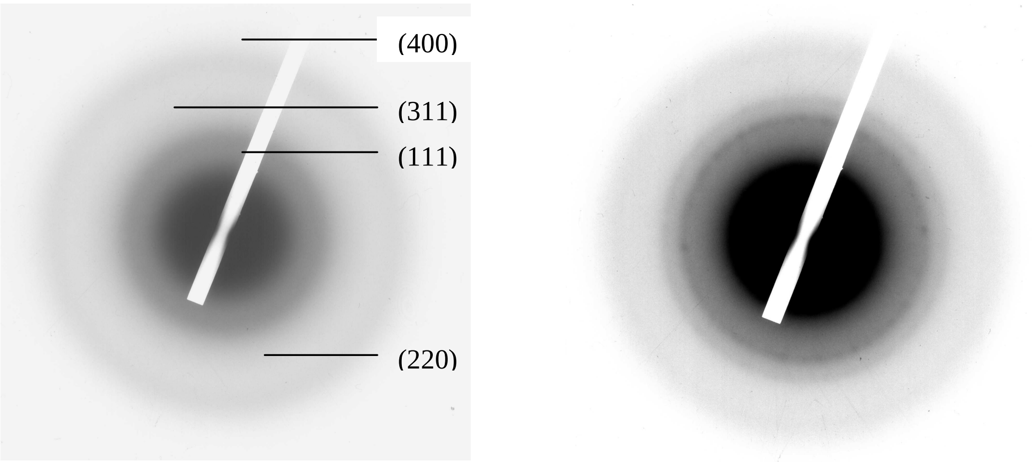
A characteristic TEM cross-section picture of the SiO_x film after annealing at 1000 ^oC for 30 min is presented in Fig. 2. At some places of the substrate `band-contours` start from the interface between the Si substrate and the oxide (see the contrast effect on Fig. 2b) demonstrating the inner stress caused by the technological steps, predominantly by annealing. The cross sectioned sample shows clearly the thickness of the SiO_x films, which for the as-deposited state was found to be 170 nm and was decreasing during annealing. As is seen in Fig. 2a, the thickness of the film annealed at 1000^{o}C for 30 min is 160 nm. These values are in very good agreement with the thicknesses obtained from the ellipsometric measurements [8], being 172 and 163 nm, respectively.



a) b)

Fig. 2. Cross-sectional TEM images, taken from two different places (a) and (b), of SiO_x/Si film-substrate structure annealed at 1000 ^{o}C for 30 min.

As it can be expected, in the sample annealed at 700 ^{o}C Si crystalline phase in the amorphous SiO matrix was observable neither in high-resolution electron microscopy image nor in its selected area diffraction patterns. On the diffraction pattern only the wide-diffuse amorphous rings appear (see Fig. 3a). In contrary to that, the selected area diffraction pattern taken from the oxide films annealed at 1000^{o}C for 30 min (Fig. 3b) exhibits clearly visible four crystalline rings beside the diffuse amorphous ones.



a) b)

Fig. 3. Diffraction pattern in the SiO_x films annealed at 700^{o}C for 30 min (a) and at 1000^{o}C for 30 min (b).

The fine structure of rings shows that they have arisen from very small Si crystallites, randomly oriented in the amorphous oxide matrix. They are also visible as small dots in Fig 2. The crystalline rings can be indexed as (111), (220), (311) and (400) diffraction lines of the bulk Si, respectively.

According to the high-resolution TEM (HRTEM) images of the films annealed at 1000°C for 30 min, the size of the crystallites is below 4 nm (see Fig. 4). In most of the cases the Si nanocrystallites have an irregular shape according to HRTEM observations. From the analysis of several HRTEM images the average size of Si nanocrystallites was found to be 3 nm. Due to the small size of the nc-Si clusters the interfaces between the Si nanocrystallites and amorphous oxide are not well-defined crystal planes producing defect centers.

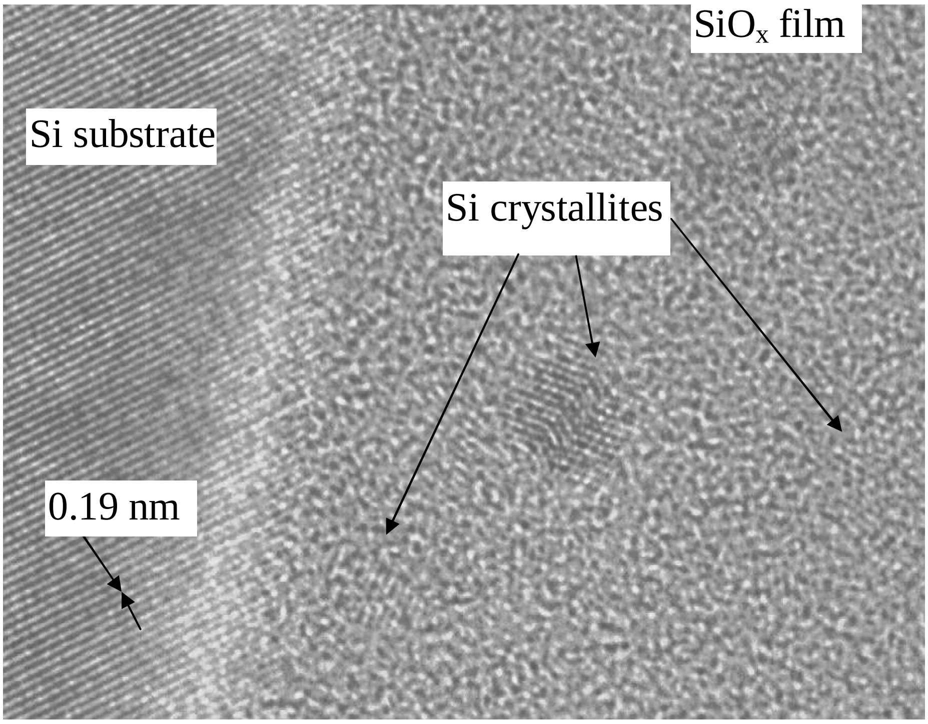


Fig. 4. High-resolution TEM picture of SiO_x film annealed at 1000 °C for 30 min.

It has been established [10,11] that at elevated temperatures SiO_x structure is not stable and the oxide decomposes into Si and SiO_2 phases which can be described as $2SiO_x \rightarrow x\ SiO_2 + (2-x)Si$.. Decomposition of SiO_x takes also place under the given annealing conditions, and, as the TEM results show, the resulting Si phase appears in small sized Si nanoclusters. In order to estimate how big are the volume fractions of the Si and SiO_2 phases in the SiO_x film, the samples were measured by spectral ellipsometry and the results were analysed by applying the effective medium approximation theory. The results show that the films are considerably dense since no voids are detected in the material. There are some volume fractions of SiO_2 with a tendency to increase with increasing the annealing temperature and time. As is seen from Table 1, a rather high fraction of SiO_2 phase is already detected in the as-deposited films. This can be explained with partial oxidation of the evaporated SiO clusters during deposition due to residual oxygen in the vacuum chamber. The effective value of the stoichiometric index is x =1.26, being close to that obtained from the IR data analysis [1].

Due to annealing the volume fraction of the SiO_2 phase increases at the expense of silicon monoxide and the stoichiometric index of SiO_x increases up to x=1.58 after annealing at 1000 °C. At lower annealing temperature (700 °C) the number of the decomposed, oxygen free Si atoms is small but it is an evidence for built-in Si nanoparticles in the oxide matrix. In the case of higher temperature, the volume fraction of the Si atoms increases and both the amorphous and crystalline phases are present in the oxide. With increasing the annealing time the number of the Si crystallites increases at the expense of amorphous state, but it still remains considerably low. This can explain why in the XRD spectra other Si crystalline peaks cannot be detected and confirms the suggestions made from the XRD results. The TEM and SE results support the observations of other researchers

[3-6] that the crystallization process depends on the size of the Si clusters and in the case of small clusters the crystallization starts at much higher annealing temperature than that usually observed for amorphous Si material, for which the crystallization process starts above 650°C [12].

Table 1. Thickness and composition of as-deposited and annealed SiO_x films.

Annealing conditions (°C, min)	Physical composition (Volume fraction of composites)				SiO_x
as-deposited film	73.7	26.3	-	-	$SiO_{1.26}$
700°C, 5 min	75.8	22.4	1.8	-	$SiO_{1.23}$
700°C, 30 min	73.4	22.7	3.9	-	$SiO_{1.24}$
1000°C, 5 min	61.3	28.2	3.2	7.3	$SiO_{1.32}$
1000°C, 30 min	36.7	49.1	2.3	11.9	$SiO_{1.58}$

4. Conclusions

Comprehensive analysis of the XRD, TEM and SE spectra data of vacuum evaporated SiO_x films have shown that annealing leads to decomposition of SiO_x, changing the film composition from $SiO_{1.26}$ for as-deposited films to $SiO_{1.58}$ for films annealed at 1000°C and with increasing volume fraction of the Si phase. The Si atoms form randomly distributed in the oxide matrix nanoclusters with average size of 3 nm, which are crystalline at the annealing temperature of 1000°C.

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