TEM study of the sol-gel oxide thin films

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This paper presents a comparative transmission electron microscopy (TEM) study of structure and morphology of different sol-gel oxide films, showing relevant structural features resulting from film deposition and subsequent annealing. We expose several details of the TEM specimen preparation, cross section and plan view and discuss the main features which can be observed using these specimens. Results on the various sol-gel film oxides, tin oxide, indium oxide, zinc oxide, hafnium oxide and others, are presented and compared, following different types of annealing used for film crystallization: furnace annealing, rapid thermal annealing and pulsed laser annealing.

Keywords: oxide sol-gel films; XTEM; electron irradiation; pulsed laser annealing

1. Introduction

The sol-gel oxide thin films are nowadays present in a large number of applications: protective coatings, surface opto-mechanical modifications, transparent oxide conductor contacts and others. The sol-gel films are obtained from various precursors, inorganic or metal-organic, using mainly two deposition methods: dipping and spinning [1].

After their deposition, the sol-gel films are amorphous and soft and contain an important quantity of solvent and precursor species. After drying the solvent traces are removed. The subsequent thermal treatment induces the densification of the amorphous structure and removes also the remaining precursor traces. At this stage, the sol-gel films have a dense amorphous structure with a high density of nanopores. The last annealing step takes place at higher temperature and induces crystallization and the final film nanostructure formation.

The microscopic structure of the sol-gel films can be studied in detail by transmission electron microscopy (TEM), from the amorphous structure state, to the final crystalline one. The plan view, cross section (XTEM), or other special methods for TEM specimen preparation, allows the complete characterization of the structure and the morphology of the sol-gel films in different annealing stages.

Some structural studies of the sol-gel films are made using scanning electron microscopy (SEM) or atomic force microscopy (AFM). These two methods are fast, but show only the surface topography of the film, which is not always directly related with the inside film structure. The TEM study is more complicated, involves more time for specimen preparation and observations, but is the only way to study the film volume structure and morphology.

The crystallization process of the sol-gel films is not similar for all oxides. There are significant differences in the final morphology and structure of different type of oxide films. Some of the amorphous structures are sensitive to the electron beam irradiation, which induces in-situ nanocrystallization. In the same time, the duration and the annealing method are very important for the final film morphology. The classical thermal (furnace) annealing (CTA), the rapid thermal annealing (RTA) and the pulsed laser annealing (PLA), are herein exemplified.

The morphology and the structure of a thick multilayer sol-gel film, obtained by multiple depositions are different for each deposited layer due to the different number of annealing time supported by the successive deposited layers. Depending on the annealing method and atmosphere, the film develops inside porosity, surface crust and also some stress field, which appears in the oxide lattice or at the interface between the deposited layers. This stress field is partially released by extended defects generation, which can appear either in the film or in the substrate.

In the present paper we expose several details of the specimen preparation and results for the several sol-gel films oxides, such as: ATO(SnO₂:Sb), ITO(In₂O₃:Sn), TiO₂, HfO₂, ZnO and BTO (BaTiO₃). We show comparatively some characteristic structural features of different sol-gel oxide films, revealed by the TEM study, and deal with the potential problems, which may appear.

2. TEM specimen preparation

TEM specimens from the sol-gel thin films deposited on glass or silicon wafers can be prepared in several ways. The most effective method is the cross section (XTEM) preparation. This technique consists in mechanical cutting of small rectangular pieces, gluing these pieces face to face with special epoxy, cutting slices with thickness of about 0.5 mm followed by mechanical polishing with different diamond powder grade to the limit of less than one micron and finally by ion milling. This process is schematically shown in Fig. 1.
In some cases, the plan view observations are necessary. In this preparation, the mechanical polishing and the ion thinning are performed only from the substrate side of the sample (see Fig.2). Function of the film thickness, the film only or the film superposed on its substrate can be observed. One of the problems of the plan view preparation from the crystallized film is the stress field developed in the film structure [2]. This stress field induces high tensions inside the film and at the film-substrate interface. This stress field relaxes when the plan view specimen is enough thin during the ion milling and the specimen can be broken and lost.

Fig. 2  Schematics of the plan view specimen preparation. Specimen section before the ion milling (a) and after the ion milling (b)

One alternative to the plan view preparation is the mechanical extraction of small fragments from the film and its substrate using a thin diamond tip [3], and deposit these fragments on a carbon copper grid. Some fragments are very thin and the obtained TEM images can show even high resolution details. This method is fast and can give information even for the film thickness if the electron microscope has a high angle goniometer.

Fig. 3 illustrates the type of images which are commonly observed using the XTEM specimens. The images are performed on a XTEM specimen prepared from an amorphous dried BiTiO3 (BTO) sol-gel film. The selected area electron diffraction (SAED) pattern in Fig. 3d shows the diffuse ring of the amorphous film structure (arrowed) superposed with the diffraction spots of the [110] zone axis of the Si substrate.

In the case of films deposited on Si [100] wafers, the XTEM specimen must be oriented in the microscope (using the goniometer stage) to align the electron beam direction parallel with the film surface. In this way, the film interface with the substrate can be observed at high resolution (see Fig. 3c) and the film thickness determination is very accurate.

3. Structure of sol-gel oxide films

3.1 ATO and ITO sol-gel films

Transparent Conducting Oxides (TCO) like ITO (In2O3: Sn) and ATO (SnO2: Sb) films can be successfully deposited on different substrates by the sol-gel method [4-11]. Data about the morphology and the structural modifications of TCO films during their drying, densification and crystallization stages were revealed by XTEM [4,9]. After deposition and drying, these films are amorphous and non-conductive. Conductivity is obtained after their crystallization. This structural transformation is a key factor for some applications and the electron microscopy observations are very effective for the study of the crystallization process. After drying of an ATO sol-gel film at a temperature of 150°C, crystalline nuclei of about 2 nm are formed embedded in the amorphous matrix, but the film remains insulator. After the classical (CTA) thermal annealing at 500°C, the film structure crystallizes and become conductor. Fig. 4 shows the structural differences between the two cases. The crystallized film has grain size in the range of 5 to10 nm, as visible in Fig. 4b. The film conductivity grows with the size of the crystalline grains [4].
During the crystallization process, a dense “crust” is formed at the film surface due to the very active surface diffusion during crystallization. The XTEM images reveal very well the successive layers in the section of multilayered films due to this crust formation for each sol-gel deposited layer [4, 5]. The rapid thermal annealing (RTA) of the ATO films leads to similar morphology as the case of classical annealing, but the structure is more uniform and the grain size smaller. The crusts between the deposited layers remain visible but have a smaller thickness compared with the CTA case, as shows in Fig. 5a.

The crust formation and evolution insight the volume of the multilayer film is exposed schematically in Fig 6. The subsequent annealing performed after each new deposited layer, induces the densification of the embedded layers by reducing the nanopore size. Because in the crust region the structure is already dense, a stress field develops at the level of the embedded crusts, which partially relaxes by lattice defects formation in the crystallite grains. Some micro-twinning defects can be observed inside the crystallites forming the crusts in multilayered films [4]. This indicates the high level of stress reached in some ATO crystallites forming the internal crusts, during subsequent densification induced by the successive annealing. This “crust” model can be applied to the sol-gel oxide films which have crystalline grain size smaller than the thickness of the deposited layer.

Fig. 3  The main type of image areas which can be observed on a XTEM (BTO) specimen:
(a) low magnification image,
(b) medium magnification image,
(c) high resolution image.
(d) SAED pattern of the film and the Si substrate in [110] orientation.

The BTO film was annealed for 10 minutes at 400°C. The film structure is amorphous and is stable under the electron beam irradiation during the HRTEM observations.

Fig. 4  High resolution (HRTEM) details of the XTEM specimen prepared from an ATO sol-gel film after drying at 150°C for 45 minutes (a) and after furnace annealing at 500°C for 45 minutes (b).
The dried amorphous film is insulator and the film annealed at 500°C is crystallized and conductor.
Low magnification XTEM images of the multilayer (5 layers) ATO sol-gel film (a) and ITO sol-gel film (b). Fig. 4a shows the comparison between the same ATO film sample annealed by RTA and CTA. (S – is the pyrex substrate, and 1 to 5 are the subsequent deposited layers). Fig. 5b shows a ITO film which has the crystallite size bigger than the similar ATO film. ITO film presents also quite big nanopores with size which decreases from the top layer to the bottom layer (arrowed a- in the top layer, b- in the middle and c at the bottom).

Schematics of the cross section of a multilayer sol-gel film morphology. The crust appears by annealing on the top of every deposited layer and remains and develops embedded in the film volume during the subsequent annealing.

Classical thermal annealing holds only for thermal resistant substrates. In the case of polymer substrates for instance, heating must be confined in the film volume. This can be obtained using excimer laser radiation in ultraviolet. If the laser photon energy is higher than the band gap energy of the oxide, the laser radiation will be absorbed in a thickness of about $1/\alpha$, where $\alpha$ is the absorption coefficient of laser radiation. This laser absorption depth in the ATO dried sol-gel films is of the order of 20 nm in the case of ArF excimer radiation ($\lambda=193$ nm).

Sol-gel film annealing using excimer lasers allows the crystallization depth control in the film thickness [12-14]. Fig. 7 shows a XTEM image of an ATO sol-gel film after laser annealing. Only the top part (about 100 nm) of the film is crystallized. Laser processing allows heating of the oxide film surface at high temperatures. However, temperatures larger than the melting point of the oxides are not useful for crystallization because the film surface becomes less smooth and the ablation process can induced.
3.2 TiO₂ sol-gel film

In Fig. 8 is shown a medium magnification XTEM image of a 500 nm thick anatase sol-gel film formed by 5 deposited layers. The morphology and the porosity of the TiO₂ sol-gel film can be better observed in the plan view specimen prepared from a monolayer deposited film as shown in Fig.9. Due to their photocatalytic properties, the doped TiO₂ film and powders obtained by sol-gel method are intensively studied [15].
3.3 HfO₂ sol-gel film and electron beam sensitivity

The HfO₂ sol-gel films have been produced on the base of ethoxide, pentadionate and chloride precursors [16]. If the annealing temperature is less than 500°C, the film remains amorphous. The resulted HfO₂ sol-gel film is very thin, with thickness of about 10 to 15 nm for each layer deposition. Multilayer film can be obtained by subsequent layer deposition after each annealing for amorphous phase densification or after deposited layer crystallization.

The crust formation is less visible in this case because the crystallization process is fast, producing large grains with inside nanopores. This feature shows that the crystallization process starts from few nuclei in the amorphous phase. The crystallization front moving fast goes around the existing pores, resulting in a quasi-coherent crystalline lattice with inside nanopores, as can be observed in Fig. 10 and Fig.11.

![Fig. 10 XTEM image of a monolayer HfO₂ sol-gel film obtained from pentadionate precursor [16,17], after crystallization by CTA annealing at 600°C for 30 minutes. The film has a thickness of about 12 nm. The size of the crystalline grains is much larger than the film thickness. The SiO₂ layer at the interface with the Si substrate is characteristic feature for the case of the HfO₂ films deposited on silicon wafers.](image)

Fig. 11 Plan view image (a) and the corresponding SAED pattern (b) of the HfO₂ sol-gel film obtained from pentadionate precursor after annealing at 600°C. The plan view image reveals a large HfO₂ crystalline grain in [111] orientation, which contains a high density of inside nanopores. The SAED pattern (b) shows diffraction spots from the HfO₂ film and the silicon substrate in [001] orientation. The HfO₂ crystallized grain contains a lot of defects related to the nanopores presence. This large crystalline grain in fact a mosaic of little disoriented nanocrystalline domains, as the angular dispersion of the (220) HfO₂ diffraction spots shows. The presence of nanopores is more visible in the plan view image.

![Fig. 12 HRTEM observation of a HfO₂ sol-gel film deposited on silicon substrate: (a) film structure after the first 10s of high resolution observations (b) the same structure after 120 s of observations under a electron density of 10 A/cm²](image)

The amorphous HfO₂ sol-gel films are very sensitive to the electron beam irradiation. The amorphous phase crystallizes under the electron beam irradiation producing a high density of nucleation sites and finally nanometric size crystallites, as shown in Fig.12. This effect is a non thermal one. The temperature rise on the specimen is low even for high density of electron current [16], if the specimen is well prepared. We expect a radiolysis character of this transformation because it happens also in time at lower electron density or lower electron beam energy. This sensitivity to the electron beam irradiation is normal for ionic materials and was not observed on sol-gel amorphous oxide as ATO, ITO or ZnO.
3.4 ZnO sol-gel films

ZnO sol-gel films have been produced from acetate precursors. Crystallization of these films takes place at more than 450°C. The multilayer morphology of these films is no more visible in the XTEM images. Fig. 13a shows some dense and less dense layers in a sol-gel ZnO multilayer film formed by 5 deposited layers. There is only tree dense level in the cross section image. This happened due to the fast growing ZnO crystallites and also due to the sintering like process. A dense layer of ZnO crystallites appear on the substrate interface and also at the film surface. Somewhere in the middle of the film appears also a dense region, which contains larger crystallites and nonpores with size of the same order of magnitude as the crystalline grain size.

The c-axis texture, which is characteristic for most of the ZnO films obtained by other methods as RF or PLD [19], does not appear normally in ZnO sol-gel film. In this case, the crystallization has a homogeneous nucleation in the ZnO amorphous phase and the orientation of the growing nucleus is uniformly distributed in space. The crystal growth process is rapid and some grains have size which is larger than the deposited layer thickness.

The mechanism which controls the crystal growth process inside the film during the subsequent annealing is similar to the sintering process but also to the Ostwald ripening one, in which a crystallite grows by surface diffusion using material from smaller adjacent grains. Inside the film is a competition between the new nucleation process in the last deposited layer and the continuum growth of the already formed crystalline grains in the previous deposited layer. This explains the absence of the crust morphology in the case of ZnO multilayer film, and also the absence of the crystalline texture.

Fig. 13  a- XTEM image of a ZnO sol-gel multilayer film (5 layer film) showing only tree level of densification. Each dense level alternates with a less dense one, which contains a high density of pores. b- SAED pattern obtained from a plan view specimen of the same ZnO sol-gel film. The equal intensity of all tree reflections rings: (100), (002) and (101) shows the absence of the texture in the ZnO film structure.

4. Conclusions

The TEM study of the sol-gel oxide films allows the complete characterization of the structure in all the stages of film elaboration, from the dried amorphous phase to the final crystalline phase. The cross section specimen preparation is the best way to obtain high resolution data about the film crystallinity and porosity and the structure of the interface with the substrate.

For sol-gel films having thickness less than 50 nm, the plan view TEM specimen preparation is interesting for film porosity determination. In the case of some amorphous oxides or mixed amorphous oxides, the HRTEM observations must pay attention to the irradiation effects in the microscope. The sol-gel oxide films are generally nanostructured and non-textured. The size of the oxide crystallites are normally in the range of 10 to 100 nm. The size of the inside nanopores depends on the total annealing time and the annealing method used for crystallization.

The multilayer deposited films show a density variation in their volume, due to the different time duration of the thermal treatment applied on the subsequent deposited layers and due to the crust formation at the surface of every deposited layer.

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References