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Thermal annealing of amorphous Ti-Si-O thin films

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Abstract

Ti-Si-O thin films were deposited using an aerosol chemical vapor deposition process at atmospheric pressure. The film structure and microstructure were analysed using several techniques before and after thermal annealing. Diffraction results indicate that the films remain X-ray amorphous after annealing whereas Fourier transform infrared spectroscopy gives evidence of a phase segregation between amorphous SiO₂ and well crystallized anatase TiO₂. Crystallization of anatase TiO₂ is also clearly shown in the Raman spectra. Transmission electron microscopy analysis indicates that anatase TiO₂ nanograins are embedded in a SiO₂ matrix in an alternated SiO₂/TiO₂ multilayer structure.

Keywords: Ti-Si-O thin films, Aerosol CVD, Multilayered microstructure, Mictamict.

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I. INTRODUCTION

Mixed titania-silica ($\text{TiO}_2\text{-SiO}_2$) amorphous films cover a wide range of achievable refractive index because of the large difference of the refractive index of the two compounds. This property is useful for the preparation of several optical devices (antireflective coatings¹, passive² or active³ waveguides, notch filter⁴). The mixed $\text{TiO}_2\text{-SiO}_2$ thin films can also be used as dielectric materials due to a high dielectric constant, a high breakdown field and a low leakage current.⁵ These films have been deposited by various physical methods such as electron beam evaporation⁶, sputtering^{5,7}, pulsed laser deposition⁸ and chemical methods such as sol gel⁹⁻¹¹ and chemical vapour deposition (CVD) with low-pressure systems^{12,13} or with assisted process (ultraviolet (UV)¹⁴ or plasma¹⁵). In a previous paper, we reported a new process to obtain Ti-Si-O films by an aerosol CVD process at atmospheric pressure¹⁶. The as-deposited films are amorphous and the relative proportions of TiO_2 and SiO_2 are controlled in function of the deposition conditions.

As previously mentioned, mixed Ti-Si-O thin films have a larger number of applications in the amorphous state. These films are also obtained as composite materials with crystallized titania embedded in silica matrix. Machida *et al.*¹⁷ reported that the addition of SiO_2 into a TiO_2 film yields optimum photoinduced superhydrophilicity. Such films with crystallized TiO_2 grains can be also obtained from amorphous Ti-Si-O films by thermal annealing.

Since TiO_2 and SiO_2 are immiscible¹⁸, any crystallization in the mixed films implies segregation or exodiffusion of Ti. The segregation phenomenon is well reported by Sankur *et al.*⁶: in codeposited $\text{TiO}_2\text{-SiO}_2$ films, TiO_2 crystallizes in anatase structure between 600 and 900°C and in rutile phase between 900 and 1100°C. The crystallization temperature as well as the crystal size depend on the initial composition of the film. The segregation mechanism is controlled by the Ti diffusion in the film.

In this paper we study the influence of thermal annealing under different gas atmospheres on the structure and microstructure of mixed $\text{TiO}_2\text{-SiO}_2$ films deposited by aerosol CVD.

II. EXPERIMENTAL

The Ti-Si-O thin films of about 100 nm thickness were deposited on Si (100) substrate using an atmospheric aerosol CVD reactor. A precursor solution was transformed in an aerosol by ultrasonic spraying and, after transport, it was deposited by pyrolysis on a heated substrate¹⁹. Titanium tetrabutoxide and di-acetoxi di-butoxisilane were used as precursors, butanol-1 as solvent and acetic acid and acetylacetone as adducts. More details on this experimental process

are reported in Refs. 16 and 20. Thermal transformations of two types of films were studied: films deposited at 550°C with a TiO₂/SiO₂ atomic ratio of 40/60 (A) with a density of 2.56 g/cm³ and films deposited at 500°C with a TiO₂/SiO₂ atomic ratio of 56/44 (B) with a density of 2.61 g/cm³. The film composition and density were obtained from X-ray Photoelectron Spectroscopy (XPS) and electron probe microanalysis. Pure TiO₂ and SiO₂ reference films were grown using the same process.

Annealing treatments were performed at different temperatures ranging from 700°C to 950°C for 1 to 12 hours in air or argon atmosphere.

X-ray diffraction (XRD) data were obtained on a $\theta/2\theta$ Siemens D500 (Bruker-AXS, Marne la Vallée, France) powder diffractometer (Cu $K_{\alpha 1}$ $\lambda=0.15406$ nm) or on a Siemens D500 (Bruker-AXS) powder diffractometer (Fe $K_{\alpha 1}$ $\lambda=0.19374$ nm) at grazing incidence angle of 3°. Fourier transform infrared spectroscopy (FTIR) measurements were performed in transmission geometry using a “BioRad” spectrometer. Raman spectra were collected using a Jobin Yvon/Horiba LabRam spectrometer (Villeneuve d’Asq, France) equipped with a liquid nitrogen cooled charge-coupled device (CCD) detector. Experiments were conducted in the micro-Raman mode at room temperature in a backscattering geometry. The 514.5 nm line of an Ar⁺ laser was focused to a spot size smaller than 1 μ m. The incidence laser power measured at the sample surface was close to 7 mW. Cross sections of Ti-Si-O thin film specimens were characterized by Transmission Electron Microscopy (TEM) using a high resolution JEOL 2010 (Tokyo, Japan). Observations were made on small fragments, obtained by scraping the thin film surfaces, deposited on copper grids coated with a carbon film.

III. RESULTS AND DISCUSSION

XRD diagrams of both types of films (atomic ratio TiO₂/SiO₂ = 40/60 and 56/44) obtained either in a classical $\theta/2\theta$ configuration or with grazing incidence showed no Bragg reflections. Either an amorphous or a nanocrystalline state below the X-ray coherence length can explain such diagrams.

FTIR absorption spectra of amorphous SiO₂, anatase TiO₂ and mixed A films before and after annealing for 1 hour at 950°C under air are shown in Fig. 1. The pure SiO₂ spectrum (Fig. 1a) presents absorption bands at 450 and 1075 cm⁻¹ attributed to Si-O-Si asymmetric rocking and stretching vibrations, respectively⁵. Absorption bands observed at 435 and 260 cm⁻¹ in the case of pure TiO₂ (Fig. 1b) are characteristic of the TiO₂ anatase crystal structure^{21,22}. For the as-deposited A film spectrum (Fig. 1c), the broad absorption band at around 440 cm⁻¹ may result

from a mixture of both Si-O-Si and Ti-O bands; the bands at 930 and 1050 cm^{-1} come from Ti-O-Si and Si-O-Si bonding, respectively⁵. After annealing (Fig. 1d), the Si-O-Si band is slightly shifted to $\sim 1060 \text{ cm}^{-1}$ and its intensity increases whereas the Ti-O-Si band nearly disappears. Despite a quite noisy signal, the absorption band around 440 cm^{-1} seems to split in two lines, at $\sim 430 \text{ cm}^{-1}$ (Ti-O stretching)¹⁴ and $\sim 450 \text{ cm}^{-1}$ (Si-O-Si asymmetric rocking). Moreover, a band is noticed at 266 cm^{-1} as in the pure TiO₂ anatase spectrum. Similar spectra have been obtained for mixed B films, only band intensities are different. These results could be explained by phase segregation, i.e. a partial (or total) separation of the TiO₂ and SiO₂ phases; TiO₂ crystallizes in anatase structure whereas SiO₂ remains amorphous. The intensity increase of the band at 1075 cm^{-1} after annealing can occur because the FTIR spectra have been obtained in transmission configuration where SiO₂ signal is provided by both the TiO₂-SiO₂ film and SiO₂ formed during annealing on the backside of the substrate.

Figure 2 shows the evolution of the Raman spectra of A and B mixed films before and after several thermal annealings at 700°C, 800°C and 950°C for 1 hour under air. Spectra of pure SiO₂ and pure TiO₂ films are also shown. It is to be noticed that the pure SiO₂/Si spectrum is identical to the Si substrate spectrum (not shown in the figure). The pure TiO₂ film spectrum contains three lines at 143, 395 and 638 cm^{-1} which are characteristic of the TiO₂ anatase phase and assigned to E_g, B_{1g} and E_g modes, respectively²².

The spectra of as-deposited mixed TiO₂-SiO₂ films do not differ from that of the Si substrate nor from the SiO₂/Si one, which is in agreement with an amorphous state and with the fact that TiO₂-SiO₂ composite films are known to stay amorphous as long as the SiO₂ atomic content exceeds 15%²³. After annealing at 700°C a small and broad band can be noticed at $\sim 151 \text{ cm}^{-1}$ for both films; its intensity is slightly stronger in B film. This band is assigned to the low wavenumber anatase E_g mode and is a sign of the beginning of TiO₂ crystallization²⁴. When the annealing temperature is raised to 800°C, the E_g line gets better defined and shifts slowly to smaller wavenumbers. After annealing at 950°C, the spectra of both films show a well-defined E_g line at $\sim 143 \text{ cm}^{-1}$ in B film and $\sim 146 \text{ cm}^{-1}$ in A film, as well as two other lines characteristic of the TiO₂ anatase phase. Whatever the annealing temperature, the Raman lines of the TiO₂ anatase phase in films with higher TiO₂ content are always sharper and slightly shifted towards lower wavenumbers in comparison with those with lower TiO₂ content.

Let us now discuss the two possible origins of the shift of the TiO₂ E_g mode from 151 to 143/146 cm^{-1} induced by the thermal treatment: a size effect or a stress effect. The increase of the annealing temperature improves the crystalline state of TiO₂ and usually causes an increase of the

TiO₂ grain size. The Raman spectrum of TiO₂ nanoparticles has been extensively studied due to the unusual broadening and shifts of the Raman lines with decreasing particle size and because the intense E_g line appears as the most sensitive line to reveal size effects. The shift towards low wavenumbers actually indicates an increase in particle size, as reported in several papers^{25,26}. The second possible origin of such a shift could be a compressive stress effect of the SiO₂ matrix on the TiO₂ nanograins. The TiO₂ spectra of the films annealed at 950°C would thus reveal a stress relaxation of the TiO₂ particles, complete in the B film as observed by the similarity between its Raman spectrum and the reference anatase spectrum, and partial in A. This can be explained by a higher compressive stress of the matrix on the TiO₂ crystallites, which are smaller in A film. Indeed, it is reported that an increase in TiO₂ content in TiO₂-SiO₂ codeposited films involves an increase in TiO₂ crystal size⁶. Our Raman results do not allow elimination of one of the two hypotheses since both size and stress effects are related each other; we will see in the following section that TEM observations rather suggest that the stress effect is dominant.

Bright field transmission electron micrographs of mixed A film cross sections and corresponding selected area electron diffraction patterns are reported in Fig. 3. The film thickness indicated on each bright field image was determined with respect to 111 lattice fringes observed on Si substrates (i.e., $d_{111} = 3.134 \text{ \AA}$). For the as-deposited sample (Fig. 3a), an amorphous SiO₂ layer of about 1.5 nm in between the thin film and the Si substrate can be identified by its average *Z* contrast lower than that of the amorphous Ti-Si-O film. Let us note that the film exhibits a speckled contrast which, along with being an effect of the transfer function of the microscope, could partly result from an unmixing of amorphous states. The corresponding electron diffraction pattern (Fig. 3b) is composed of the reflections of the Si substrate oriented along a [110] zone axis and of a broad diffuse ring centered at about 1.8 \AA^{-1} . After annealing at 950°C under air for 1 hour, crystalline particles of anatase TiO₂ of less than 10 nm size and embedded in a SiO₂ matrix are observed (Figs. 3c and 3d). The anatase structure is unambiguously identified from a comparison between the diffracting rings observed on the corresponding electron diffraction pattern (Fig. 3d) and a simulation of the anatase diagram. Curiously, the TiO₂ particles appear to be arranged in a multilayered structure parallel to the (001) surface of the silicon substrate. Six strata of TiO₂ particles can be observed in this case. Because of the annealing treatment under air, an important oxidation of the Si substrate has occurred giving rise to an increase of the SiO₂ interface layer thickness (up to 45 nm), probably by ionic oxygen and electronic diffusion. This thick SiO₂ layer can explain the intensity increase of the Si-O-Si band at $\sim 1075 \text{ cm}^{-1}$ observed in the corresponding FTIR spectrum (Fig. 1d).

Such an oxidation effect can be avoided by using argon instead of air during the annealing treatment (Fig. 3e). In this case, however, smaller crystalline TiO₂ particles of less than 5 nm size are formed. A multilayered microstructure is also observed but with more strata of TiO₂ particles (11 or 12 strata). The identification of the anatase structure shown in Fig. 3f corresponds to a selected area of a plane view of the thin film. After a second annealing at 950°C for 11 hours, only a few changes are observed (Figs. 3g and 3h); the average size of TiO₂ has slightly increased of about 15 % and, as observed in the thicker part of the cross section, the number of strata of TiO₂ particles has reduced to six.

The formation of these alternated TiO₂-SiO₂ multilayers or strata in Ti-Si-O thin films after annealing can result from the regular Ti diffusion in the mixed films in order to obtain stress relaxation, as observed in Raman spectra. The number of TiO₂ strata varies between six and twelve, depending on the initial film thickness, on the grain size and the gas atmosphere during annealing.

All these results related to mixed TiO₂-SiO₂ thin films prepared by aerosol CVD agree with those reported in literature for films obtained by other deposition techniques. Song et al¹¹ prepared TiO₂-SiO₂ films by sol-gel from starting solution with Si/Ti ratio equal to 1/1. After thermal treatment at temperatures up to 950°C, they observed anatase TiO₂ nanocrystallites embedded in a SiO₂-rich matrix. Our Raman results show that the incorporation of SiO₂ in a TiO₂ film raises the crystallization temperature of the TiO₂ anatase phase as reported by Giauque et al⁷ et by Sankur et al⁶ on mixed TiO₂-SiO₂ films prepared by reactive magnetron sputtering and electron beam evaporation, respectively.

IV. CONCLUSIONS

Complementary techniques were used to study the influence of thermal annealing on the structure and microstructure of 100 nm thick TiO₂-SiO₂ films deposited by aerosol CVD at atmospheric pressure.

Although the films remain X-ray amorphous at annealing temperatures as high as 950°C, FTIR and Raman spectroscopy indicate that TiO₂ crystallizes in anatase structure from temperature at around 700°C. More details about the phase segregation and film microstructure are given by TEM analysis. Especially, anatase TiO₂ nanograins embedded in a SiO₂ matrix are observed as an alternated SiO₂/TiO₂ multilayered structure. The particle size and the number of layers are strongly dependent upon air or argon atmosphere during thermal annealing: about 5

and 10 nm size, and 6 and 12 layers, respectively, for films annealed at 950°C for 1 hour. In agreement with Raman results, such a multilayered structure may favour a stress relaxation in the films. All these results indicate that TiO₂-SiO₂ films belong to the quasi binary Mictamict alloys (mictamict: mictos-amictos in Greek, means miscible-immiscible)⁷.

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Figure captions

Fig. 1: Typical FTIR spectra of (a) amorphous SiO₂ film, (b) anatase TiO₂ film, a mixed TiO₂-SiO₂ film (A: atomic ratio TiO₂/SiO₂ = 40/60), (c) as-deposited and (d) annealed for 1 hour at 950°C under air.

Fig. 2: Raman spectra of amorphous SiO₂ film, anatase TiO₂ film, mixed TiO₂-SiO₂ films with atomic ratios TiO₂/SiO₂ = 40/60 (A) and 56/44 (B) as-deposited and annealed at 700°C, 800°C and 950°C for 1 hour under air.

Fig. 3: Bright field transmission electron micrographs and selected area diffraction patterns of a mixed TiO₂-SiO₂ film (A: atomic ratio TiO₂/SiO₂ = 40/60) (a, b) as-deposited, (c, d) annealed for 1 hour at 950°C under air, (e, f) annealed for 1 hour at 950°C under argon, (g) annealed for 12 hours at 950°C under argon. The insets in (a), (c) and (e) correspond to high resolution images of the Si/film interface. A multilayer microstructuring is shown in (h).

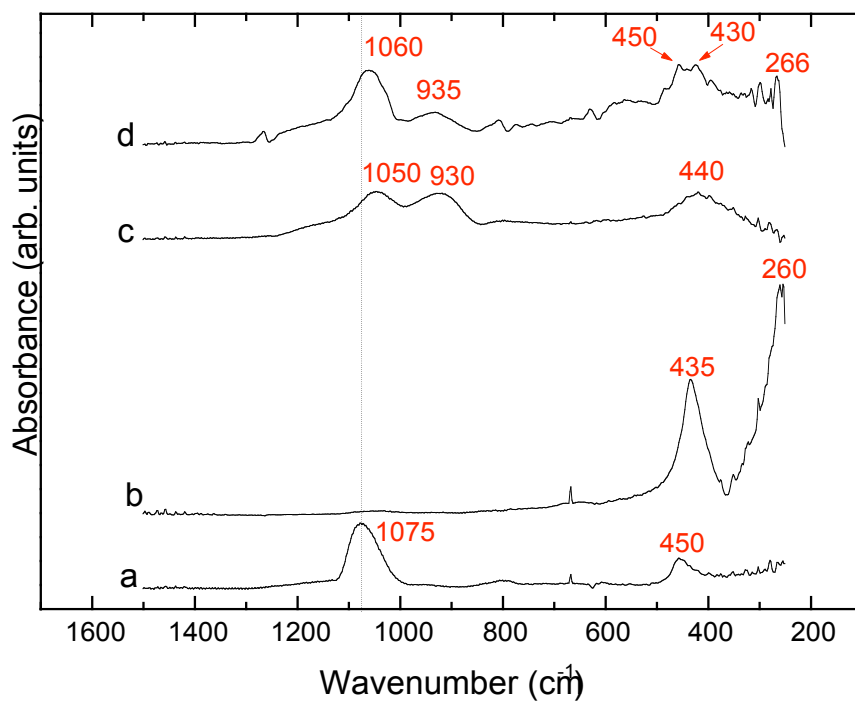


Fig. 1

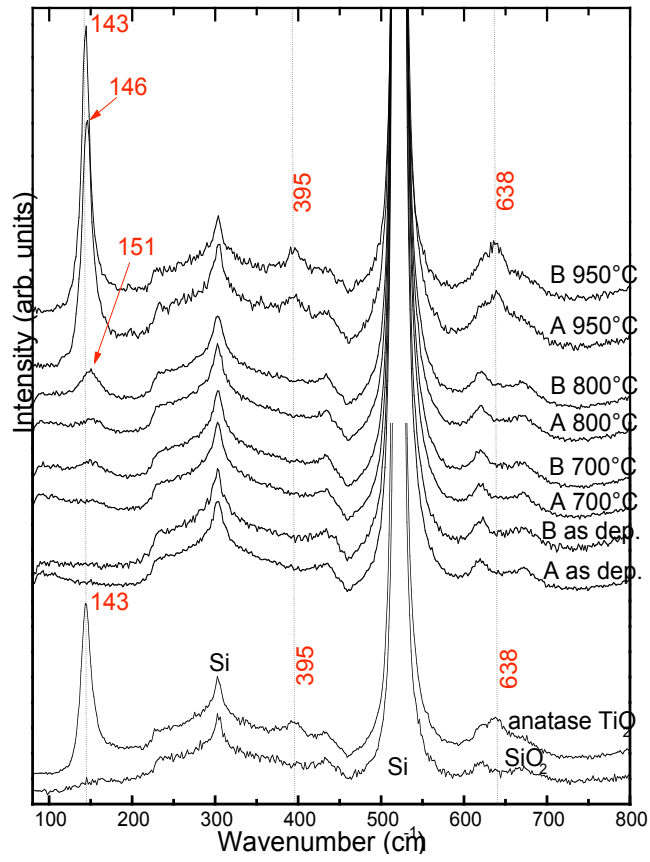


Fig. 2

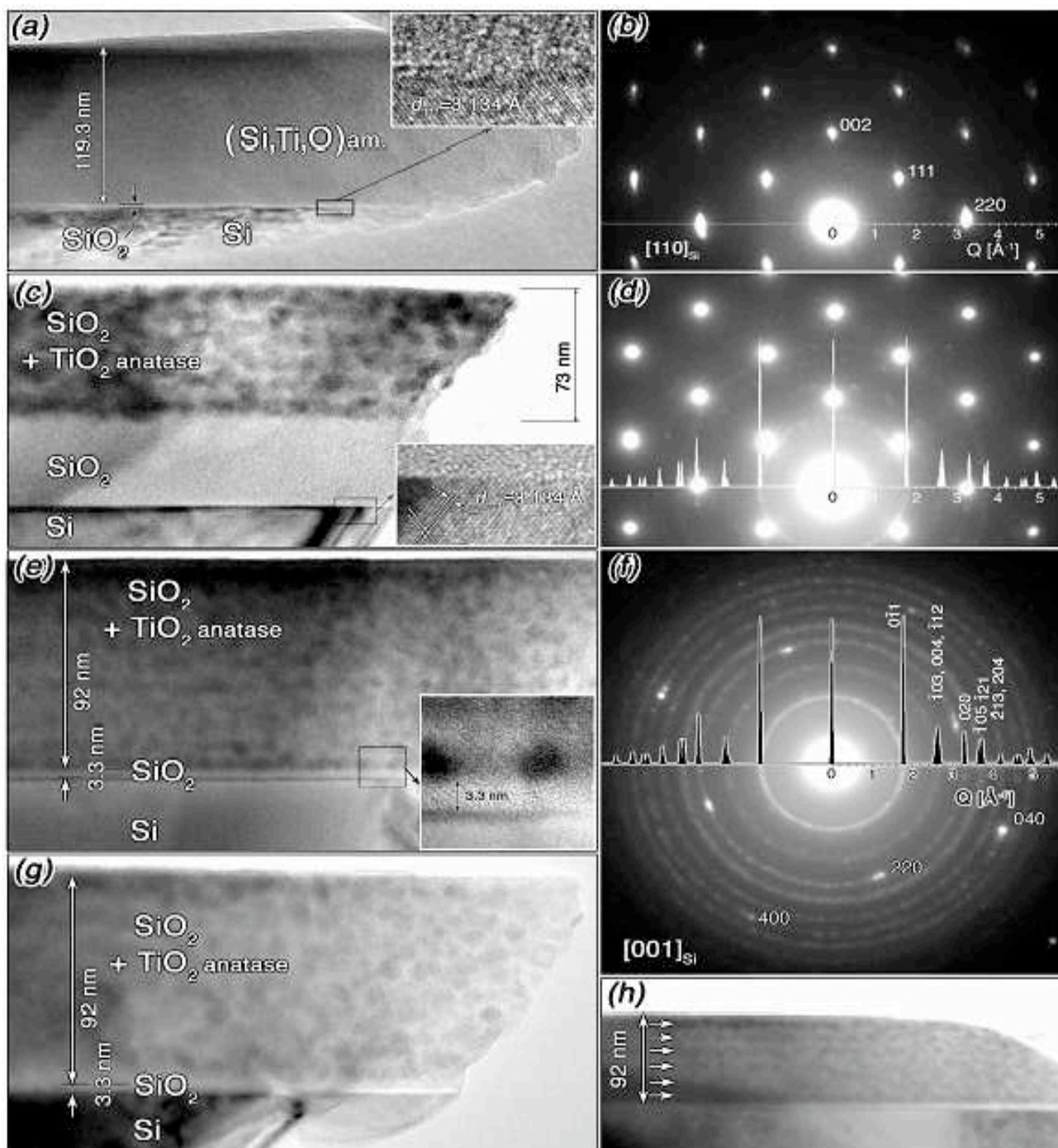


Fig. 3