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On the microstructure of $TiHfO_x$ thin films

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Transition metal oxides, whose optical band gap might be modified by doping or manufacturing using two (or more) oxides with different band gaps, are good candidates for host matrices in luminescent devices. This paper presents structural properties of $TiHfO_x$ thin films and analysis of dependence of their optical properties on thin film structure. In order to examine the microstructure of manufactured thin films the X-ray diffraction (XRD) and atomic force microscopy (AFM) were applied. The optical properties of manufactured thin films were investigated by optical transmission method in the spectral range from 200 to 1400 nm.

Keywords: multicomponent oxide, thin film, magnetron sputtering, hot target.

1. Introduction

Thin films of multicomponent oxides fabricated from transition metal oxides with different band gaps and nanocrystalline structure have recently been studied for various applications [1]. Transition metal oxides are good candidates for host matrices in luminescent devices [2–4]. The aim of this work was to study the microstructure of thin films of oxides consisting of the titanium dioxide (TiO_2) and the hafnium dioxide (HfO_2).

The hafnium dioxide thin films are insulators which can be used in corrosion protection and as insulating layers [2, 5]. Because of good thermal and mechanical stability HfO_2 is a promising material for optical coatings, as well [6]. The HfO_2 films are transparent in the infrared, visible and in the ultraviolet region of the light spectrum up to ca 240 nm [7].

2. Experimental procedure

Thin films of Ti-Hf oxides were fabricated by the low pressure hot target reactive magnetron sputtering (LP HTRS) [8]. Mixed Ti-Hf composition of sputtered material

was assured by placing Hf sheets (Aldrich, USA, purity 99.5%, 0.5 mm thick) on the surface of titanium (purity 99.99% and 3 mm thick) disc (mosaic target). The ratio of the amount of components in the whole material coming from the mosaic target was estimated to be Ti:Hf = 46.7%:53.3%. The rate of the thin film deposition was kept at about 0.1 nm/s. This caused the deposited thin films to be homogeneous with the grain sizes in the range of nanometer.

Thin films were deposited onto monocrystalline (100) oriented silicon wafers (300 μm thick). After the deposition, selected samples were annealed at a temperature of 1000 K for 4 hours in air. The thickness of the manufactured films measured by the optical interference method with Hg (551 nm) filtered lamp was 485 nm.

3. Microstructure and optical properties

In order to examine the microstructure of the manufactured thin films, X-ray diffraction (XRD) was applied. The measurements were performed on DRON-2 powder diffractometer using Fe-filtered $K\alpha$Co radiation. The size of crystallites was measured at the full width at half maximum (FWHM) of the peaks on XRD patterns using Scherrer equation corrected for instrumental and spectral line broadening and $K\alpha_1\alpha_2$ doublet.

To complete the structural analysis, selected samples were examined by means of PicoForce (Veeco) atomic force microscope (AFM) working in contact mode.

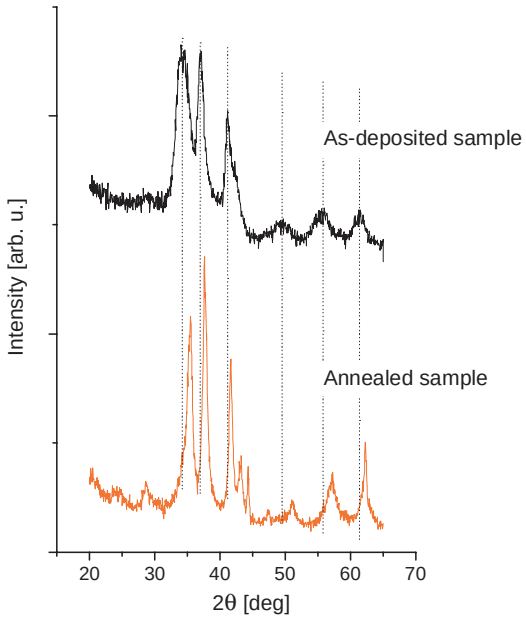

Fig. 1. XRD patterns of as-deposited and annealed thin films of mixed composition of TiO_2-HfO_2 (the atomic ratio of components in sputtered target Ti:Hf = 46.7%:53.3%) deposited onto monocrystalline (100) oriented silicon wafers.

The optical properties of manufactured thin films were investigated by optical transmission method in the spectral range from 200 to 1400 nm in "so-called" bright configuration. The fundamental absorption edge of manufactured thin films was determined from the normalized transmission spectra.

In Figure 1, XRD patterns of as-deposited and annealed thin films were presented. In the case of as-deposited sample strong but wide diffraction lines were found. The sample consists of fine crystalline $HfTiO_4$ phase. This phase is typical in the case of film component of Ti:Hf atomic ratio amounting to 46.7%:53.3%, obtained from sputtering parameters and individual velocity [9]. Heat treatment enhanced the crystallinity of the thin films and well-shaped lines of the orthorhombic $HfTiO_4$ appeared. The grain sizes were in the range of 30 to 40 nm.

As can be seen from Fig. 1, a preferred orientation of crystallites has occurred in the samples after annealing. The shift of the diffraction peaks for the annealed samples to higher scattering angles may suggest a stress relief in the layer.

In Figure 2, the AFM images of as-deposited $HfTiO_4$ thin film surface have been presented. As can be seen, the surface of thin film consists of square-shaped nanocrystallites. The 3D images show clearly that the crystallites have the shape of domed nodules. The thin film surface exhibits the homogenity in the crystallite size

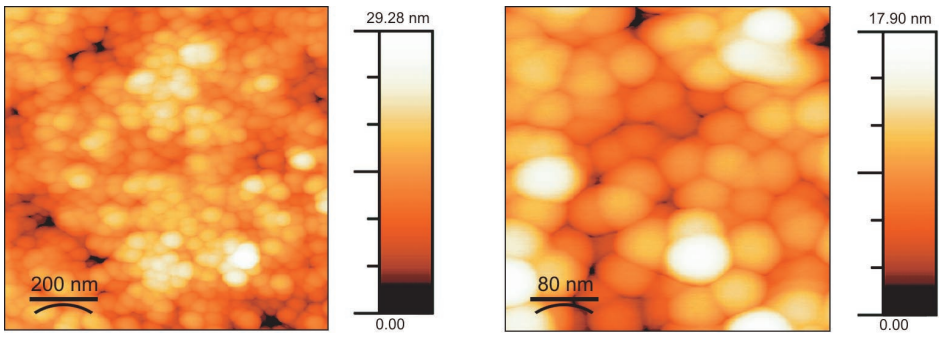

Fig. 2. AFM images of $HfTiO_4$ as-deposited surfaces on silicon wafer.

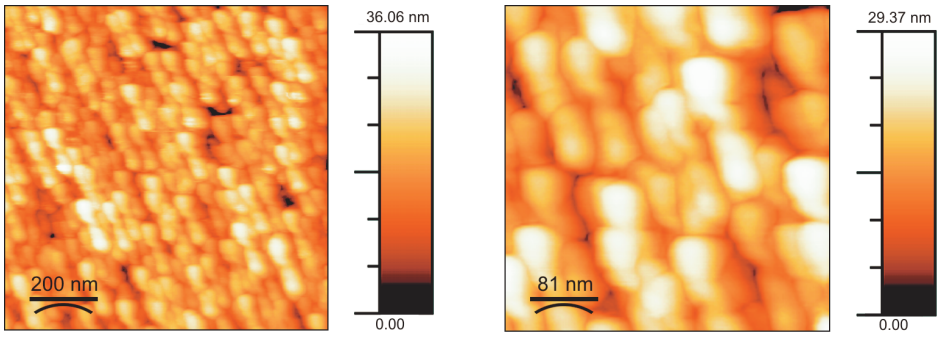

Fig. 3. AFM images of $HfTiO_4$ annealed surfaces on silicon wafer.

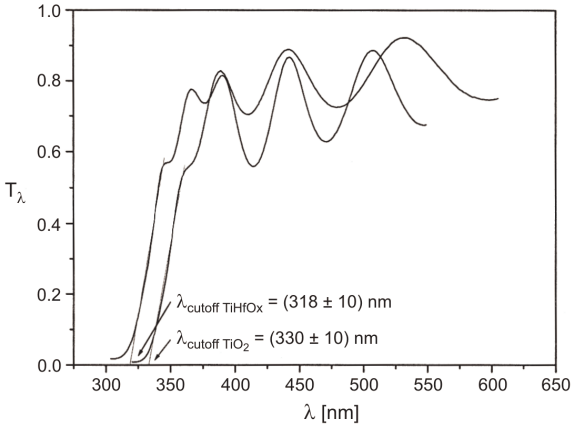

Fig. 4. Normalized transmittance spectra of as-deposited $HfTiO_4$ and TiO_2 thin films.

distribution. As one can see from Fig. 2, as-deposited $HfTiO_4$ thin film consisted of nanosize crystallites with a dimension of about 50 to 80 nm.

In Figure 3, the AFM images of $HfTiO_4$ surface in the case of annealed samples have been presented. It can be seen that after annealing the nanocrystalline thin films exhibit the high degree of order. They contain lengthwise-shaped crystallites with preferred orientation, which is in agreement with XRD examinations. It can be observed from Fig. 3 that the dimension and arrangement of crystallites are actually homogeneous on the whole sample surface. The crystallites are about 120 nm in length and 60 nm in width. As one can notice in 3D images, the shape of nanocrystallites is better distinguished than in the case of as-deposited samples. This leads to a conclusion that the nanocrystalline structure of the layers results from annealing process.

In Figure 4, the normalized transmission characteristics $T_\lambda(\lambda)$ of the $HfTiO_4$ and TiO_2 thin films have been presented. The fringes visible in the transmittance spectra result from the multiple interference of the light reflected from the two optical interfaces: air–thin film and thin film–substrate. Extrapolation of the linear parts of the spectra in the short wavelength range yields the position of the fundamental absorption edge, *i.e.*, λ_{cutoff} = 318 nm ± 10 nm and λ_{cutoff} = 330 nm ± 10 nm, for $HfTiO_4$ and TiO_2 thin films, respectively. It shows the blue shift of the fundamental absorption edge for $HfTiO_4$, as compared to pure TiO_2 (prepared in similar technological conditions, 415 nm thick).

4. Conclusions

Thin films of $TiHfO_x$ were fabricated by LP HTRS with the atomic ratio of Ti:Hf equal to 46.7%:53.3%.

The employment of XRD and AFM method let us state that the nanocrystalline structure of the layers had a high ordering grade. A shift in diffraction peaks to the

range of higher scattering angles suggests the stress relief inside the film due to heat treatment.

Optical examinations have shown that the fundamental absorption edge (λ_{cutoff} = 318 nm) was shifted towards ultraviolet region, as compared to pure TiO_2 (λ_{cutoff} = 330 nm).

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