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Investigation of microstructure, micro-mechanical and optical properties of $HfTiO_4$ thin films prepared by magnetron co-sputtering

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ABSTRACT

Titania (TiO_2) and hafnium oxide (HfO_2) thin films are in the focus of interest to the microelectronics community from a dozen years. Because of their outstanding properties like, among the others, high stability, high refractive index, high electric permittivity, they found applications in many optical and electronics domains. In this work discussion on the hardness, microstructure and optical properties of as-deposited and annealed $HfTiO_4$ thin films has been presented. Deposited films were prepared using magnetron co-sputtering method. Performed investigations revealed that as-deposited coatings were nanocrystalline with $HfTiO_4$ structure. Deposited films were built from crystallites of ca. 4–12 nm in size and after additional annealing an increase in crystallites size up to 16 nm was observed. Micro-mechanical properties, i.e., hardness and elastic modulus were determined using conventional load-controlled nanoindentation testing. the annealed films had 3-times lower hardness as-compared to as-deposited ones (~9 GPa). Based on optical investigations real and imaginary components of refractive index were calculated, both for as-deposited and annealed thin films. The real refractive index component increased after annealing from 2.03 to 2.16, while extinction coefficient increased by an order from 10^{-4} to 10^{-3}. Structure modification was analyzed together with optical energy band-gap, Urbach energy and using Wemple–DiDomenico model.

1. Introduction

Metal oxides with precisely defined properties are of increasingly important role in the development of modern technologies. Materials, which have been the subject of many publications in the recent years are titanium dioxide (TiO_2) and hafnium dioxide (HfO_2). Such interest is caused due to the many advantages of these oxides, e.g., high transparency, very good thermal, chemical and mechanical stability or high photocatalytic activity [1–3]. HfO_2 and TiO_2 are also well known materials used in many electronics and optical applications. They are wide band-gap materials with good electrical insulating properties and high relative permittivity ($\varepsilon \sim 20$ for HfO_2 and 50 for TiO_2) [3]. Relatively high refractive index (about 2.1 and 2.3 at 550 nm), high transparency and high chemical stability makes them attractive for optical coatings industry. In modern optical coatings, it is more often required from such coatings to fulfill also other functions, e.g., protective. This, in turn, imposes certain requirements regarding their mechanical properties, especially hardness, abrasion/scratch resistance and flexibility.

In the current state of the art many publications about hard and so-called superhard materials can be found and the vast majority of these materials are used as wear resistant coatings for various tools. Up to now, only few studies in the literature have been devoted to research of materials applied as optical coatings in relation to their protective properties. According to the literature, TiO_2 is a material whose hardness is in the range of 2–13 GPa [4–14]. Such a large range of values of this parameter is due to the fact, that the hardness depends not only on the type of material, but also on manufacturing method, crystalline structure and crystallites size of thin films. Besides TiO_2, hafnium dioxide is also one of the oxide materials, which exhibits relatively high hardness and is applied in the construction of optical coatings [15–18]. This material has good thermal and mechanical stability, high dielectric constant and good thermodynamic stability [15]. Moreover, HfO_2 has relatively high refractive index and a wide band gap (Eg ~ 5.8 eV), which makes it transparent over a wide waveband from ultraviolet (up to ca. 240 nm) to mid-infrared with low optical

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absorption and dispersion [19]. Its high hardness, which is dependent from the type of deposition method, can be equal even up to 9.5 GPa [20–21]. Studies in the field of hard films, e.g., [22] show that increased hardness may be easier obtained by manufacturing of multicomponent materials. However, in the subject literature, up to now there is a lack of reports regarding research of mechanical properties of thin film optical coatings manufactured in the form of mixtures, e.g., based on titanium and hafnium oxides. Titania and hafnia may form different types of compounds with different properties. For example, appropriate atomic ratio of titanium to hafnium in the film allows on receiving of $HfTiO_4$ structure, which is a stable compound that could combine advantages of TiO_2 and HfO_2. However, up until now, only a few studies in the literature have been devoted to researching this kind of compound, e.g., [23–25], but none of them reports about its micro-mechanical properties.

In this paper, the properties of $HfTiO_4$ thin films prepared by reactive magnetron sputtering process have been described.

2. Experimental

Thin films were prepared by reactive magnetron sputtering method. During deposition metallic Ti and Hf targets were co-sputtered in oxygen (99.999% purity). During the process the oxygen pressure was kept below 10^{-2} mbar and the magnetron was powered by DPS unipolar pulse power supplier with the voltage amplitude up to 1800 V. The thin films were deposited on silica (SiO_2) substrates and their thickness was about 650 nm.

After deposition samples were additionally annealed at 800 °C using Nabertherm tubular furnace equipped with a quartz tube. The samples were annealed under synthetic air flow through the furnace tube. Annealing temperature of prepared thin films was chosen in order to observe possible transformation of the TiO_2-anatase phase to the TiO_2-rutile phase if they were present in the mixed HfO_2–TiO_2 oxide compound.

The elemental composition of thin films was investigated with the aid of a FESEM FEI Nova NanoSEM 230 scanning electron microscope equipped with EDS spectrometer (EDAX Genesis) with a resolution of 1 nm. The EDS, used for measurements was calibrated for quantitative analysis. Therefore, it is accurate for qualitative analysis form approximately 0.1 at.% and for quantitative analysis from ca. 1 at.% element content.

Structural properties of prepared coatings were determined by X-ray diffraction (XRD) method. For the measurements, Siemens 5005 powder diffractometer with Co Kα X-ray (l = 1.78897 Å) was used. The correction for the broadening of the XRD instrument was accounted and the crystallite sizes were calculated using Scherrer's equation [26]. The XRD studies were performed using Co lamp filtered by Fe (30 mV, 25 mA), step size was equal to 0.02° in 2q range, while time-per-step was 5 s.

The surface topography was examined by Veeco (PicoForce) atomic force microscope (AFM), which was working in ambient air. Scans of the surface diversification have been done in contact mode. Using AFM such physical properties of the surface as distribution of the nanocrystalline grains as well as the topography were determined. For the analysis of experimental data WSxM software was used [27].

Mechanical properties, such as hardness and Young's modulus, were evaluated by a Hysitron Triboscope Nanomechanical Test System fitted with a Berkovich indenter tip (a three-faceted pyramid). The micro-mechanical property values of each film were determined by conventional load-controlled nanoindentation testing. For nanoindentation tests, 1.5 mN force was suitably matched to the physical thickness of the thin films. For each loading/unloading cycle, the applied load value was plotted with respect to the corresponding position of the indenter. The resulting load-displacement curve was then analyzed to determine the micro-mechanical properties of the sample material according to Oliver and Pharr formula [28,29]. Values of hardness and reduced elastic modulus were averaged from 10 indentations.

Within the framework of this work the influence of additional annealing on optical properties of deposited films was analyzed. Based on the results of transmission and reflection measurements such parameters like refractive index (n) and extinction coefficient (k) were determined. Measurements of as-deposited and annealed films were carried out in range of 350–1000 nm, at 30° angle of incident light, for S and P polarization, by NKD-8000 (Aquila Instruments) spectrophotometer. The calculations of thickness, refractive index and extinction coefficient were performed using the Drude–Lorentz model. For further analysis the optical energy band-gap, Urbach energy were calculated and the Wemple–DiDomenico model [30] was used.

3. Results and discussion

3.1. Microstructure and micro-mechanical properties

In the as-prepared thin films the amount of hafnium and titanium was equal to 51 at.% and 49 at.%, respectively. The X-ray microanalysis was performed three times in different places on the sample. The EDX spectrum showing the lines from Ti and Hf elements is presented in Fig. 1.

In Fig. 2 the results of XRD measurements of as-deposited and annealed at 800 °C thin films are shown. It was found that in case of both samples $HfTiO_4$ phase was present. According to the phase diagram [31], such compound can be received when the atomic ratio of Ti–Hf is in the range from 36 at.% to 53 at.%. For the as-deposited samples (Fig. 2a) strong and wide diffraction lines were observed, which testify about the nanocrystalline nature of their microstructure. The average crystallites sizes were in the range of 4.3–12 nm. Additional post-process annealing caused enhancement of the crystallinity of the thin films that resulted in occurrence of narrower and more intense diffraction lines (Fig. 2b). Heat treatment also resulted in an increase of the crystallites sizes up to ca. 9.9–16.0 nm.

For as-deposited thin film a considerable shift of the diffraction peaks related to the $HfTiO_4$ phase towards lower angle (2θ) indicates presence of a tensile stress. After additional annealing narrowing of the recorded peaks was noticed. Moreover, peaks were shifted towards higher diffraction angles, which were close to the values reported for the bulk material [32]. This effect can be assigned to the stress reduction in the $HfTiO_4$ structure. The type of stress occurring in the investigated thin films was determined on

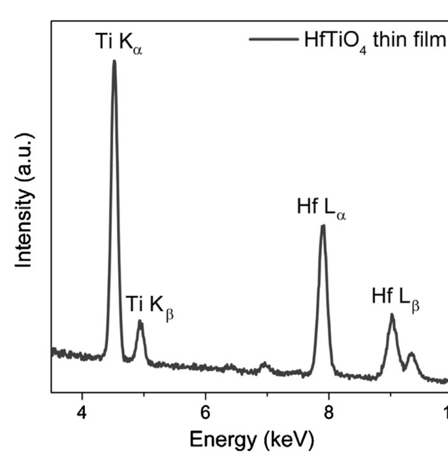

Fig. 1. EDS spectrum of as-prepared $HfTiO_4$ thin films.