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Study of Structure Densification in TiO_2 Coatings Prepared by Magnetron Sputtering under Low Pressure of Oxygen Plasma Discharge

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Current work presents results of studies on structural and optical properties of the TiO_2 thin films prepared by reactive magnetron sputtering. Oxide thin films were deposited from metallic targets using oxygen gas only instead of usually used mixture of Ar–O_2. Additionally, an increased amplitude of unipolar pulses powering the magnetron has been applied. It is shown that all prepared coatings were stoichiometric and by changing only the discharge voltage it is possible to influence the resulting structural phase and optical properties of prepared thin films. Depending on conditions of magnetron powering, TiO_2 thin films had either the anatase structure with refraction index $n = 2.1$ ($\lambda = 500$ nm) or a high temperature stable rutile structure with $n = 2.52$ ($\lambda = 500$ nm).

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1. Introduction

Fabrication of optical coatings with excellent optical properties means, in general, that the prepared thin film should be characterized by either low or high refraction index, high transmission or high reflection in a selected part of the light spectrum, low absorption, low internal stress, dense structure and smooth surface. Combination of thin films with different optical properties (multi-layered systems) allows us for the preparation of many different kinds of coatings, which could be grouped in mirrors, antireflectors, beam splitters and filters. For deposition, different techniques are applied, of which magnetron sputtering (MS) is one of the most powerful and appropriate for industrial purposes.

Magnetron sputtering allows for the deposition of various types of materials from metals through semiconductors to oxides [1, 2]. Thin films are deposited by sputtering a source material (metallic or ceramic) by ions of a working gas. Since for metal layers, the metallic target is sputtered by ions of neutral gas (usually argon), preparation of oxides from metallic target requires the presence of an additional reactive gas — oxygen. Selection of the O_2/Ar ratio is dependent on many factors. If O_2 pressure is too low, deposited thin film is more “metallic” and becomes opaque. Transition from metallic to oxide mode occurs upon increasing of O_2 partial pressure in gas mixture and usually a sharp hysteresis loop — transition mode is present [2]. However, as the oxygen ratio increases, deposition rate decreases due to target oxidation. As a compromise, for preparation of stoichiometric oxides with high deposition rate the transition mode is usually chosen.

In recent years, the goal for many researchers was to obtain more dense, hard, chemically stable and well adhered thin films. Thin films with nanocrystalline structure have been shown to have improved mechanical properties (hardness) [3, 4].

In vapor deposition techniques “densification” of the thin film is related to the energy of the process at the thin film formation location [5]. Increase in energy makes the film densification [6] and could be realized by: increase of substrate temperature, increased ion flux that imparts the nuclei at the substrate and increased kinetic energy of the ions [5, 7]. For the MS, by increasing the power to the target, high density plasma can be obtained and the energy is in the range from tens to hundreds eV. High power, in order to avoid the target overheating and as a consequence its melting, may be reached by applying the power in pulses [3, 7, 8].

Since the mid-1990s, many modifications of conventional MS, including so-called “hot target sputtering — HTS”, have appeared [9, 10]. Main modification of the HTS process concerned an enhancement of target temperature by limiting its cooling which opened new possibilities of fabrication of novel materials with unique properties like nanocrystalline structure and much more homogeneous composition.

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High-energy argon ions used in a standard MS processes reduce the energy at the site of the thin film formation and may cause film damage. But up to now there have been no reports on their elimination from the sputtering processes and applying only oxygen as a working and reactive gas. The advantages of the absence of the argon ions are elimination of collisions which cause variations in the paths of sputtered material particles on the way between the target and substrate [11, 12]. The first publications on the subject occurred in 2002 and concerned the properties of thin TiO_2 layers deposited in the oxygen atmosphere at low pressure magnetron sputtering process [13, 14]. In 2005, Pamu et al. [8] and in 2008 Toku et al. [15] offered a comparative analysis of the properties of thin layers deposited in argon–oxygen atmosphere with different oxygen content and in oxygen atmosphere only [15]. The results showed that in case when the oxygen content did not exceed 30%, the layers exhibited atanase type structure whereas with increasing oxygen content, two-phase structure of atanase-rutile was likely to develop. Furthermore, with the increase of oxygen content from 20% to 100% the grain size reduced from *ca.* 50 nm to *ca.* 25 nm.

In the present work, the structural and optical properties of thin TiO_2 layers deposited by two modified magnetron sputtering methods, namely low pressure hot target reactive sputtering (LP HTRS) and high energy reactive magnetron sputtering (HE RMS) have been compared.

2. Experimental

The processes applied by the authors termed as LP HTRS [16] and high HE RMS [12] employed combination of different operation modes used in modified sputtering processes [1, 7, 9]. In both processes thin films of TiO_2 were prepared under low pressure (0.1 Pa) of oxygen (purity 99.99%) plasma using titanium disc (purity 99.99%) 100 mm in diameter and 3.8 mm thick.

Plasma processes with the pressure lower than 10^{-1} Pa are called low pressure sputtering [3, 8, 17–19]. The main advantage of low pressure is longer mean free path that allows oxygen ions to bombard the surface with higher energy. As a result, small grains can be formed. However, low sputtering pressure simultaneously decreases the ion flux and thus the deposition rate.

The target was mounted on the magnetron cooling plane using 1.5 mm thick and 20 mm in diameter copper spacer for rising thermal resistivity. The power released in plasma allowed heating of the target surface (hot target) close to the melting point. Heating the target close to the melting point allows additional "hot" electrons to be delivered to the plasma as a result of thermoemission. The collision of thermoemitted electrons with neutral oxygen atoms at the outer area of the target plays an important role in ionization process, allowing an increase in the process energy. The increase in target temperature favoured stability of discharge in transition mode and allowed one to obtain almost stoichiometric thin films [9, 12, 16]. The magnetron was powered by pulsed power supply working in the unipolar mode with 165 kHz sinusoidal pulses grouped with 1.6 kHz. The magnetron powering was chosen so that the sum of the oxygen delivered to the chamber could react with sputtered metallic species. The target to substrate distance was 90 mm, and the substrates during deposition were heated up to 570–680 K by radiation heaters. No additional substrate potential was used. The difference between LP HTRS and HE RMS is that some changes in the design of the applied supplier were introduced [20] and as a result the amplitude of applied sinusoidal pulses was increased from -1.2 kV for LP HTRS to -1.5 kV for HE RMS.

Applied modifications enable preparation of dense and stoichiometric thin films. However, simultaneous reduction of deposition rate has been noticed. When deposited atoms have enough energy they can migrate through the substrate and condense where potential energy is lower. Increasing nucleation energy is assured by increasing the energy of incoming ions. Ion bombardment during the film growth enhances its densification and stimulates the crystal growth at the substrates. The thin films were deposited onto silica (SiO_2) substrates. For microstructure investigations of prepared thin films, X-ray diffraction (XRD) and atomic force microscope (AFM) were applied.

Optical properties of manufactured thin films were investigated using preconfigured optical spectrophotometer working in the spectral range from 200 nm to 1000 nm.

3. Results and discussion

The XRD patterns recorded for thin films prepared by LP HTRS displayed the anatase phase with crystallites about 20 nm in an average size and preferred (101) orientation. Application of pure oxygen plasma as compared to conventional process results that prepared thin films were characterized by dense, homogeneous and stoichiometric structure [16, 17]. However, in case of HE RMS, XRD investigations reveal presence of fine-crystalline rutile structure with preferred (110) plane orientation [21, 22]. Average size of crystallites was lower than 10 nm. Thus it is concluded that, as compared to LP HTRS, structure densification occurs. Atomic force microscopy investigations also confirm this conclusion (Fig. 1). The number of grains observed per 1 μm^2 increases in HE RMS about four times (from *ca.* 115 to 425).

The initial size of deposited particles plays an important role in further structural transformation kinetics. As it was shown by Gribb et al. [23], the rate of transformation from the anatase to the rutile increases as size of nanocrystals decreases. So growth in the form of small nanocrystals creates favorable conditions for the rutile growth. In the case of LP HTRS thermodynamically stable rutile was gained after additional post-deposition annealing at 800 °C. Heating for 2 h results in the formation of rutile crystallites 40 nm in average size [16].

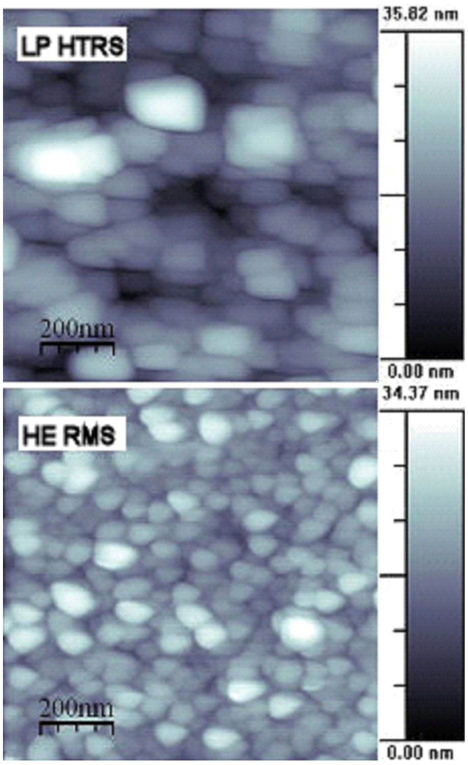

Fig. 1. AFM images of TiO_2 thin films prepared on SiO_2 by LP HTRS and HE RMS.

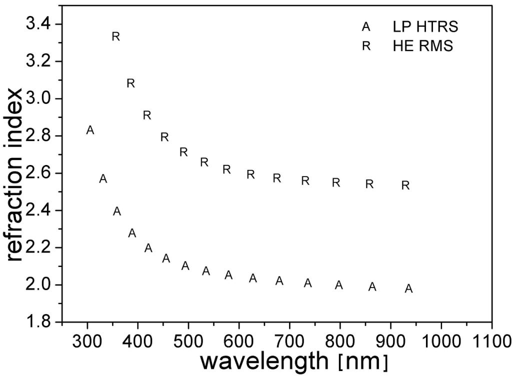

Fig. 2. Spectral characteristics of refraction index for the thin films prepared by LP HTRS and HE RMS. A stands for the anatase film and R for the rutile.

Initial growth of the rutile during deposition needs higher energy per nucleus that must be delivered in the place of the thin film creation. In the HE RMS method as opposite to LP HTRS the driving force for nucleation in the rutile form is increased amplitude of unipolar pulses supplying the magnetron source. It allowed an increase in the energy of ions that sputter the target, but also to impart sufficient energy to the nucleus from the oxygen ions reaching the substrate.

Spectral characteristics of refraction index (n) have been presented in Fig. 2. As it could be expected, the TiO_2 thin films with the anatase (A) structure had lower n values than those recorded for the TiO_2-rutile (R) thin film, which are close to the bulk rutile. Similar results have been reported by Okimura [3] for thin films prepared in modified rf magnetron sputtering.

Obviously, higher n-value observed for the rutile is the result of a different crystal structure. However, in Ref. [8] the effect of the composition of argon–oxygen mixture on optical characteristics of deposited thin TiO_2 layers was discussed. With the increase in oxygen content from 20% to 100% in Ar/O_2 mixture, the refractive index decreases from *ca.* 2.2 down to *ca.* 1.85 approaching the values of n even much lower than for the annealed layers [24].

4. Summary

In the work the means of deposition of dense films using low-density plasma with only oxygen as a working gas was shown. To our knowledge, there have been no similar results presented in the literature so far. Depending on the conditions of power supplying as-deposited thin films have either the anatase (LP HTRS) or dense bulk-like rutile crystal structure (HE RMS).

On the other hand, low density but homogeneous thin films (i.e. porous) are required for many gas-sensitive applications for which LP HTRS method would be more appropriate. By varying only the conditions of power supplying, it was possible to prepare thin films with a different optical density. Therefore that could be useful for preparation of multilayered coatings with the same material.

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