STRUCTURAL AND MORPHOLOGICAL INVESTIGATIONS OF TiO₂ SPUTTERED THIN FILMS

Ivan Hotový — Andrea Pullmannová — Martin Predanocy — Juraj Hotový — Vlastimil Řeháček — Thomas Kups — Lothar Spiess

TiO₂ thin films were prepared by dc reactive magnetron sputtering in a mixture of oxygen and argon on silicon and oxidized silicon substrates. The effect of post-deposition annealing (300, 500 and 700 °C for 8 h in air) on the structural and morphological properties of TiO₂ thin films is presented. XRD patterns have shown that in the range of annealing temperatures from 300 to 500 °C crystallization starts and the thin film structure changes from amorphous to polycrystalline (anatase phase). EDX measurements revealed that post-deposition annealing has affected the oxygen concentration in the film very slightly.

Keywords: TiO₂ thin films, dc magnetron sputtering, structure, morphological properties

1 INTRODUCTION

It is well known that the two crystallization phases of TiO₂, anatase and rutile, have very different optical and photocatalytic properties. TiO₂ with an anatase structure has a superior photocatalytic property compared to rutile TiO₂ while rutile shows the preferred antireflective and dielectric properties. TiO₂ has a variety of interesting applications, such as solar cells [1], as a photocatalytic material [2] as well as a gas sensor [3–7]. It is one of the most promising gas-sensing materials due to its high temperature stability, harsh environment tolerance and catalytic properties [8]. For this application, TiO₂ is used in anatase phase that features lower resistance and higher responses to gases than rutile phase, which is stable at higher temperatures. The gas-sensing properties of metal oxides are more or less related to the material surface, its high porosity and a nanostructure with small particles. Also, these properties can be essentially improved by doping of their surfaces by catalytic metals. Reactive magnetron sputtering belongs among fabrication techniques, which facilitates the control of particle properties such as size and composition on a nanometre scale, allows tight control over critical process parameters and so contributes greatly to the reproducibility of the nanostructure films.

In this study, the influence of post-annealing in the 300 to 700 °C range on the structural (XRD), composition (EDX) and morphological (AFM) properties of TiO₂ sputtered thin films was investigated.

2 EXPERIMENTAL DETAILS

The TiO₂ thin films were prepared by dc reactive magnetron sputtering from a Ti target (4 inch diameter, 99.99% purity) at oxygen partial pressure of 0.1 Pa on both silicon and oxidized silicon substrates in a mixture of oxygen and argon. A sputtering power of 600 W was used. Both argon inert and oxygen reactive gas flows were controlled by mass flow controllers. The total gas pressure was kept at 0.5 Pa. To investigate the influence of the annealing temperature the samples were post-annealed at 300, 500 and 700 °C for 8 hours in dry air. The crystal structure was identified with a Theta-Theta X-ray diffractometer (XRD) D 5000 with a Goebel mirror in grazing incidence geometry with Cu Kα radiation. Chemical composition of the TiO₂ thin films was determined using a FEI XL30 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer based on a silicon detector (EDAX) and a S-UTW-Window operating at 10 kV acceleration voltage. The surface morphology was observed by atomic force microscopy (AFM) using NT-MDT Solver under normal air conditions in the non-contact mode.

3 RESULTS AND DISCUSSION

For structural and morphological analysis, sets of as-deposited and samples annealed at temperatures 300, 500 and 700 °C were prepared. Figure 1 presents the XRD
The diffraction patterns in the range of 2θ where the diffraction peaks were observed. It was found that the prepared TiO$_2$ films had not only an amorphous but also a polycrystalline structure. The XRD diagrams of the as-deposited and annealed at 300 °C TiO$_2$ films showed that the films were only amorphous, since no diffraction peaks were observed. On the other hand, the diffraction patterns from samples annealed at 500 and 700 °C show the presence of diffraction peaks from the (101) and (200) planes of the tetragonal anatase TiO$_2$ lattice, as referred in the PDF 00-021-1272 file. The crystallization of TiO$_2$ in the anatase phase is improved, as it results from the increasing of the intensity of the diffraction lines with increasing annealing temperature. Our findings are in accordance with Tian et al [9] whose XRD observation revealed that only anatase phase was formed in TiO$_2$ films prepared by electron beam evaporation and annealed at different temperatures. As reported in the literature [10], TiO$_2$ films thermally treated at temperatures below 300 °C are randomly oriented and amorphous. Gyorgy et al [11] also obtained TiO$_2$ anatase single phase thin films by pulsed laser deposition. Sicha et al [12] prepared TiO$_2$ films by dc reactive magnetron sputtering, as in our case, and found that anatase phase always was formed at low substrate temperature.

Chemical analysis of prepared TiO$_2$ thin films was performed by energy dispersive X-ray spectroscopy (EDX). EDX spectra were acquired from different sites of the as-prepared and the annealed samples and then were averaged. X-ray counts per second (cps) were normalized to the silicon peak in order to suppress the influence of the samples thickness and unequal measurement conditions. Besides the major Kα silicon peak originating from the substrate, additional peaks were observed, attributed to oxygen Kα and Ti Kα as well as Ti Kβ ones (Fig. 2). EDX spectra of all investigated samples have revealed the presence of titanium and oxygen atoms in the thin layers and thus formation of TiO$_2$ thin films was confirmed. The presence of carbon in the EDX spectra is due to a thin carbon film sputtered on top of the samples for SEM investigation. On the basis of comparing the intensities of O and Ti Kα peaks of as-prepared and annealed samples, the effect of annealing on oxygen concentration in thin layers can be determined. Post-deposition annealing has affected the oxygen concentration very slightly: we observed a tendency of a small decrease of oxygen content in the layers, which can be explained by out-diffusion of oxygen during the annealing process [13]. Exact determination of Ti:O ratio is not possible since the examined TiO$_2$ layers are too thin and thus only a small amount of the signal acquired by EDX is attributed to the TiO$_2$ layer, while a major part of the signal comes from the silicon substrate.
The two and three dimensional AFM images taken at a scan area of $2 \mu m \times 2 \mu m$ (Fig. 3) represent the surface morphology of the TiO$_2$ thin films. After acquiring the AFM images, they were subjected to a flattening procedure using the NOVA image processing software. According to a quantitative analysis of the roughness deduced from AFM measuring (Table 1), the values of average roughness ($R_a$), root mean square (RMS) and coefficients of kurtosis ($R_{KU}$) changed in relation to the annealing conditions. The AFM topography of the as-deposited and annealed TiO$_2$ films at 300 and 500°C revealed that the film surface is rather smooth and compact (Fig. 3a-3c). From Table 1 we can see that the values of $R_a$ and RMS of these samples follow a similar decreasing tendency. A significant difference occurs at temperature of 700°C, where the film surface exhibits a higher roughness and clear grains can be seen (Fig. 3d). This also indicates that the grain growth on the film surface is completed at 700°C annealing and is in accordance with the XRD observation. A quantitative roughness analysis confirmed that the process of post-deposition thermal annealing at 700°C increased the values of $R_a$ and RMS of the sample, indicating its good polycrystalline structure at the surface.

It was found that as-deposited samples and those annealed at 300°C had significantly higher coefficients of kurtosis $R_{KU}$, which means that these samples have infrequent extreme deviations of the measured height. This is clearly seen as spikes in the 3D picture of the samples (Fig. 3a-3b). Annealing at higher temperatures caused that these spikes were suppressed and so the samples annealed at 500 and 700°C exhibited a surface without such spikes.

### 4 CONCLUSIONS

The influence of post-annealing (300, 500 and 700°C for 8 h in air) on the properties of TiO$_2$ sputtered thin
films was investigated. The annealing of the TiO$_2$ films has an important effect on the thin film structure; in particular, crystallization starts at temperatures between 300 °C and 500 °C without diffusion of oxygen. This process has a significant influence on the structural and morphological properties of TiO$_2$ thin films. EDX measurements revealed that post-deposition annealing has affected the oxygen concentration in the film very slightly. The AFM topography of the as-deposited and annealed films at 300 and 500 °C showed that the film surface is rather smooth and compact. A significant difference occurs at temperature of 700 °C, where the film surface exhibits a higher roughness and clear grains were observed. Further studies are in progress to show the sensing properties and their improving by means of doping with different elements.

Acknowledgements

This work has also been supported by the Slovak Research and Development Agency under the contract No. VVCE-0049-07 and No. APVV-0655-07 and by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences, No. 1/0553/09 and PPP programme of DAAD No. D/08/07742 and D/06/07398.

REFERENCES


Ivan Hotový received his MSc in Electronics from the Slovak University of Technology in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 1994. He is a scientific worker and lecturer at Department of Microelectronics, FEIT STU. His current research interests include the development of gas sensors, magnetron sputtering of metal oxide films and plasma etching of compound semiconductors.

Andrea Pullmannová received her MSc in Microelectronics from the Slovak University of Technology in Bratislava in 2006. Her current interest is concerned with electrical characterization of gas-sensing structures based on thin metal oxide films.

Martin Predanocy received his MSc in Microelectronics from the Slovak University of Technology in Bratislava in 2009. He is a PhD student in Department of Microelectronics, FEIT STU. His current research interests include characterization of electrical, optical and structural properties of gas-sensing materials and the development of gas sensors.

Juraj Hotový received his MSc in Microelectronics from the Slovak University of Technology in Bratislava in 2009. He is a PhD student in Department of Microelectronics, FEIT STU. His current research interests include characterization of electrical, optical and structural properties of gas-sensing materials and the development of gas sensors.

Vlastimil Reháček received his MSc in Nuclear Chemistry from the Comenius University in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 2005. He is a scientific worker in Department of Microelectronics, FEIT STU. His current research interests include the development of voltammetric sensors, gas sensors and photolithography.

Thomas Kups received his Diploma in 2001 in the Department of Physics and his PhD in 2006 in the Department of Physics and Astronomy from the Friedrich-Schiller-University Jena, Germany. Since 2006, he is a scientific researcher at the Technical University Ilmenau. His recent research focuses on the transmission electron microscopy investigations of III-Nitrides, metal-oxides and SiC.

Lothar Spiess is a Professor at Department of Materials Technology, Technical University of Ilmenau. His interest is concerned with material microanalysis and semiconductor processing.