XPS characterization of TiO$_2$ layers deposited on quartz plates

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Abstract. TiO$_2$ layers for gas sensing applications were obtained by Liquid Phase Deposition (LPD). The layers were deposited on gold-coated piezoelectric quartz crystals. The surface structure, morphology and chemical properties were analysed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). SEM showed that the layers were porous and composed of uniform crystalline grains. XPS indicated them to be non-stoichiometric.

1. Introduction

Gas sensors play an important role in detecting, monitoring and controlling the presence of low concentrations of hazardous and poisonous gases in the atmosphere [1]. In this context, ammonia detection and monitoring at a trace level are required since this compound is used as a raw material in many industrial processes such as production of fertilizers, plastics, explosives, pulp and paper, power generation, food processing or as pollution control material.

Semiconductor oxides in the form of thin films are widely employed as low-cost sensing elements for the detection and monitoring of hazardous gases [1, 2]. For that reason, intensive research was performed on the selectivity and sensitivity of different metal oxide films for impedance-based ammonia measurement [3-8]. However, the metal-oxide semiconductor based sensors generally operate at temperatures above 200°C, which leads to reduced long term stability. The advantage of the acoustic sensors is their ability to work at room temperature, which reduces the power consumption of the device and permits safer detection of flammable gases.

The present work is aimed at developing acoustic sensors for registration of NH$_3$ in the atmosphere. For that purpose, resonator structures are created by deposition of sorption TiO$_2$ layers on quartz plates. The morphology and the chemical composition of the films were studied by scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

2.1. Film preparation and deposition

TiO$_2$ thin films were prepared by the Liquid Phase Deposition (LPD) method [9]. Metal oxide or hydroxide thin films were obtained by means of ligand-exchange (hydrolysis) equilibrium reaction of metal-fluoro complex species (MF$_x$($x-2n$) and F$^-$ consumption reaction with boric acid (H$_3$BO$_3$) in the treatment solution, (MF$_x$($x-2n$) being hydrolyzed with water following the ligand-exchange equilibrium reaction:
\[ MF_{x-2n}^{(x-2n)^-} + nH_2O \leftrightarrow MO_{x-n} + xF^- + 2nH^+ \] (1)

The equilibrium reaction was shifted toward the right-hand side by the addition of boric as an F\(^-\) scavenger, which readily reacted with F\(^-\), forming a stable complex as follows:
\[ H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O \] (2)

The addition of the F\(^-\) scavenger leads to consumption of free F\(^-\) ions and accelerates the ligand-exchange reaction.

The sensors were prepared from 15 MHz AT-cut polished quartz crystal disks, 8 mm in diameter, on both sides of which gold or silver electrodes of 4 mm in diameter were fabricated. Before coating, the crystals were to be free from impurities and contaminations. The crystals with Au electrodes were cleaned with isopropyl alcohol. Then the disks were immersed in a solution of 0.1 M (NH\(_4\))\(_2\)TiF\(_6\) and 0.2 M H\(_3\)BO\(_3\) acid at 50 \(^\circ\)C to produce thin TiO\(_2\) films. The films were annealed at 500K for an hour.

2.2. Characterization of TiO\(_2\)/quartz

The composition and chemistry of the TiO\(_2\) layers were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in a VG ESCALAB II system using AlK\(_\alpha\) radiation with an energy of 1486.6 eV. The binding energies (BE) were determined with an accuracy of ±0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The changes in composition and chemical surrounding in the depth of the films were determined on the basis of the areas and binding energies of Ti2p, O1s, Si2p and Au4f photoelectron peaks (after linear subtraction of the background) and Scofield’s photoionization cross-sections. The depth profiles were obtained by ion etching of the films with 3 keV Ar\(^+\) ions and a current density of 10 \(\mu\)A/cm\(^2\).

The surface morphology of the sorption layers was examined by scanning electron microscopy (SEM) using a JEM-200CX electron microscope.

3. Results and Discussion

3.1. Structural characteristics of the film.

X-ray diffraction (XRD) revealed that the as-deposited layers were amorphous. Even after annealing at 500 K, peaks of TiO\(_2\) (anatase) phase were not detected. This is in accordance with [10] where the transformation to anatase with presence of a large amorphous band in the X-ray spectrum was observed at temperatures above 600 K.

The morphology of the TiO\(_2\) films was examined by SEM. The SEM images of TiO\(_2\) layers in the regions of the gold electrode and quartz plate are shown in Fig.1. The thin film is porous and composed of uniform crystalline grains. The layer deposited onto the Au electrode consists of grains with an average size of 100 - 150 nm. The part of the film grown on the quartz consists of larger microcrystallites with an average size of 200 nm. This result suggests that the thin film prepared is suitable for fabricating gas sensors because its porosity ensures a large surface area for gas sorption.

Figure 1. SEM image of the surface the TiO\(_2\) film deposited on: (a) gold electrode, (b) quartz.
3.2 Chemical composition of the films

The Ti2p spectra of the as-deposited and annealed at 500 K TiO$_2$ layers are shown in Fig. 2. The as-deposited film exhibits Ti2p photoelectron peaks with a slight asymmetry at the lower binding energy side of the peaks. Further, the spectrum of the film does not show a strong satellite at 14 eV from Ti2p3/2 peak which is characteristic of TiO$_2$. The position of the Ti2p3/2 peak at 459.1 eV and the shoulder at 458.0 eV indicate the presence of Ti$^{3+}$ and Ti$^{4+}$ oxidation states [12, 13]. The O1s spectra show a main peak at 530.6 eV and a shoulder at ~532.1 eV. The peak at 530.6 eV is assigned to oxygen bound to tetravalent Ti ions.

![Figure 2. Ti 2p and O1s core level spectra of the surface of the TiO$_2$ layers.](image)

The small shoulder at 532.1 eV implies that the surface is partially covered with hydroxide OH groups [14,15]. The Ti2p photoelectron spectra obtained after annealing of the sorption layer at 500 K (Fig. 2, upper spectrum) show a Ti2p$_{3/2}$ peak at 459.1 eV. The observed peak position, the doublet separation between the 2p$_{1/2}$ and 2p$_{3/2}$ peaks of ~5.7eV and the strong satellite at 14 eV from the main peak are characteristic of TiO$_2$. The shape and binding energy of the O1s peak are similar to that of as-deposited layers and could also be deconvoluted in the same two components. Fig. 3 shows the element distribution in the depth of the as-deposited TiO$_2$ layer on a quartz plate performed by Ar$^+$ ion sputtering. The stoichiometry of the film established on the basis of the O/Ti intensity ratio is TiO$_{1.86}$. The detection of Si before Au in the depth profile implies that the oxide layers deposited on the surface of the gold electrode are thicker than that on the quartz surface.

![Figure 3. XPS depth profiles of TiO$_2$ film: (a) as-deposited, (b) annealed at 500 K.](image)
The depth profile of the annealed TiO$_2$ film reveals that the thickness of the film decreases after the thermal treatment. Probably this is due to compression of the oxide layers.

4. Conclusions
TiO$_2$ layers were prepared by LPD on gold-coated quartz crystals. SEM study evidenced that the deposited layers possess a porosity suitable to fabricate gas sensors. XPS showed that the thin films are substoichiometric (TiO$_{1.86}$). After annealing at 500 K, the binding energy and the shape of the Ti2p peaks became characteristic of the Ti$^{4+}$ oxidation state. The gas sensing properties and selectivity of the films for registration of NH$_3$ will be further investigated.

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References
[1] J. Janata, M. Josowicz, D. M. De Vancy, Chemical Sensors, 1994, *Anal. Chem.* **66** 207R-228R.
[2] P. Moseley, B. Tofield, 1989, *Solid state gas sensors*, Bristol, Adam Hilger.
[3] A. Teeramongkonrasmee, M. Sriyudthsak, 2000, *Sens. Actuators B* **66** 256–259.
[4] Y. D. Wang, X. H. Wu, Q. Su, Y. F. Li, Z. L. Zhou, 2001, *Solid-State Electron.* **45** 347–350.
[5] T. Zhang, Y. Shen, R. Zhang, X. Liu, 1996, *Mater. Lett.* **27** 161–164.
[6] Y. Shimizu, T. Okamoto, Y. Takao, M. Egashira, 2000, *J. Mol. Catal. A* **155** 183–191.
[7] O. K. Varghese, D. Gong, W. R. Dreschel, K. G. Ong, C. A. Grimes, 2003, *Sens. Actuators B* **94** 27–35.
[8] K. K. Makhija, A. Ray, R. M. Patel, U. B. Trivedi, H. N Kapse, 2005, *Bull. Mater. Sci.* **28** (1) 9–17.
[9] S. Deki, Y. Aoi, Y. Asaoka, A. Kajinami, M. Mizuhata, 1997, *J. Mater. Chem.* **7** 733.
[10] A. Ahmad, J. Thiel, S. I. Shah, 2007, *J. of Physics: Conference Series* **61** 11–15.
[11] U. Diebold, 2003, *Surf. Sci. Reports* **48** 53-229.
[12] A. Sandell, M. P. Andersson, Y. Alfredsson, M. K. J. Johansson, J. Schadt, H. Rensmo, H. Siegbahn, P. Uvdal, 2002, *J. Appl. Phys.* **92** (6) 3381-3387.
[13] A. Sandell, M. P. Andersson, M. K. J. Johansson, P. G. Karlsson, Y. Alfredsson, J. Schadt, H. Siegbahn, P. Uvdal, 2003, *Surf. Sci.* **530** (1-2) 63-70.
[14] J. Pouilleau, D. Devilliers, H. Groult, P. Marcus, 1998, *J. Mater. Sci.* **32** 5645.
[15] A. Iwabuchi, C. Choo, K. Tanaka, 2004, *J. Phys. Chem. B*, **108** 10863-10871.