SOLID-STATE SOLUTIONS
OF TiO$_2$–SnO$_2$ AND SrTiO$_3$–BaTiO$_3$

K. Zakrzewska

Institute of Electronics, University of Mining and Metallurgy
Al. Mickiewicza 30, 30-059 Kraków, Poland

M. Radecka, P. Pasierb, M. Bućko

Department of Inorganic Chemistry, University of Mining and Metallurgy
Al. Mickiewicza 30, 30-059 Kraków, Poland

E. Urbaniec and J. Janas

Faculty of Foundry Engineering, University of Mining and Metallurgy
Al. Mickiewicza 30, 30-059 Kraków, Poland

Thin films of TiO$_2$–SnO$_2$ and SrTiO$_3$–BaTiO$_3$ are deposited by rf sputtering. The crystallographic and optical properties near the band gap absorption are investigated as a function of film composition. Systematic displacement of the fundamental absorption edge shows different behaviour for amorphous and polycrystalline samples. Results are discussed in terms of the influence of the substitution on the local environment of Ti ion and Me–O distances. Application of XANES and EXAFS is proposed for the studies of solid-state solutions.

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1. Introduction

Transition-metal oxides that crystallize with the rutile (TiO$_2$) and perovskite (SrTiO$_3$, BaTiO$_3$) structures represent an important class of materials. Their electronic properties are known to be highly sensitive to impurities, minor changes in stoichiometry and ambient gas atmosphere. The application of these materials to gas and humidity detection is one of the recent issues [1–4].

Although many studies of the crystallographic and electronic properties of transition-metal rutiles and perovskites have been reported in the past, little is known concerning their intermediate solid solutions. It is believed that modification of the electronic structure resulting from substitution by aliovalent additions at Ba/Sr and Ti atomic sites would affect the interaction mechanism with
gaseous atmospheres thus leading to improvement in sensor performance, e.g., cross-sensitivity.

In this work, we present the results of crystallographic and optical studies on TiO$_2$–SnO$_2$ and BaTiO$_3$–SrTiO$_3$ thin films grown by rf sputtering. These two systems have many similarities, resulting from the same Ti–O octahedral coordination which predominantly influences the band gap structure. The fundamental absorption edge of TiO$_2$ rutile (3.3 eV) is close to that of SrTiO$_3$ (3.35 eV) and BaTiO$_3$ (3.25 eV) indicating that this edge is due to the optical transitions between 2p oxygen and 3d titanium states with little admixture of Sr and Ba wave functions [5]. The basic difference between these two systems is the fact that SrTiO$_3$–BaTiO$_3$ forms a continuous solid solution over the whole concentration range while the phase diagram of TiO$_2$–SnO$_2$ exhibits a miscibility gap [6, 7]. The tendency of TiO$_2$ and BaTiO$_3$ thin films to grow in the amorphous state further prevents the conventional methods of analysis such as XRD from being used in the studies of solid solutions. Therefore, it seems that the proper approach to this problem would be to combine the optical methods such as absorption/reflection measurements with EXAFS and XANES in order to investigate the influence of the local environment of metal sites on the electronic structure of these solid solutions.

2. Experimental

Thin films of TiO$_2$–SnO$_2$ were deposited by rf reactive sputtering from mosaic metal targets. Oxide targets were used in the case of SrTiO$_3$–BaTiO$_3$ films. Film composition was varied in a wide range by changing the target coverage area. The chemical composition of samples was determined by X-ray electron microprobe and Rutherford backscattering (RBS). Polycrystalline ceramics were prepared as standards for further studies.

X-ray diffraction measurements with Cu filtered radiation were performed in a step and scan mode (2θ = 0.02 deg, 8 sec per step).

A spectral dependence of the absorption coefficient was derived from the transmission/reflection spectrophotometric measurements in a wavelength range of 250–2200 nm.

3. Results and discussion

As confirmed by the XRD analysis, SrTiO$_3$ and SnO$_2$ crystallize even when deposited onto substrates at 473 K. The increased amount of Ba in SrTiO$_3$ and that of Ti in SnO$_2$ lead to a film amorphization. Post-deposition annealing at 973–1073 K in air develops the TiO$_2$ rutile and BaTiO$_3$ perovskite structure. The lattice parameters continuously increase in both cases: (a) when Ti is substituted by Sn in TiO$_2$–SnO$_2$ and (b) when Sr is substituted by Ba in SrTiO$_3$–BaTiO$_3$ thin films, as shown in Figs. 1 and 2. This remains in good agreement with the results reported in literature [8, 9].

The changes in interplanar atomic distances are accompanied by considerable displacements in the fundamental absorption edge (Fig. 3). However, as shown previously [10], one may observe the shifts in the fundamental optical transitions in the opposite direction for amorphous and polycrystalline samples of the same composition. This effect was already reported for TiO$_2$ thin films doped with
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Fig. 1. The lattice parameters $a$ and $c$ of the tetragonal rutile as a function of TiO$_2$ content in TiO$_2$–SnO$_2$ solid-state solutions. The preferential growth of Ti-rich TiO$_2$–SnO$_2$ thin films makes it impossible to determine $c$.

Fig. 2. The interplanar spacing $d_{hkl}$ as a function of Ba/(Sr+Ba) atomic ratio in SrTiO$_3$–BaTiO$_3$ thin films after annealing.

niobium and was attributed to the different distortion of Ti coordination shell as confirmed by EXAFS studies [11]. Similar results obtained for SrTiO$_3$–BaTiO$_3$ thin film solid solutions suggest that the positive displacement (towards higher photon energies) with the increased Ba content in amorphous samples results from the contraction of the Ti–O bond length. In the case of well-crystallized samples,
Fig. 3. Spectral dependence of the absorption coefficient $\alpha$ for amorphous and polycrystalline thin films of SrTiO$_3$–BaTiO$_3$.

this displacement becomes negative (towards lower photon energies) which agrees with the band structure studies that predict a lower band gap for BaTiO$_3$ than that for SrTiO$_3$ [12].

TiO$_2$–SnO$_2$ thin films always show a positive displacement of the fundamental absorption edge upon substitution of Ti by Sn. The reason for this is a higher band gap of SnO$_2$ than that for TiO$_2$ [10]. Moreover, the material with a higher band gap is always grown in the polycrystalline state.

4. Conclusions

SrTiO$_3$–BaTiO$_3$ and TiO$_2$–SnO$_2$ thin films can be grown easily by rf sputtering. However, their state of crystallization depends on the film composition. Post-deposition annealing develops the rutile structure in the case of TiO$_2$–SnO$_2$ and the perovskite structure for SrTiO$_3$–BaTiO$_3$. SrTiO$_3$–BaTiO$_3$ solid solutions are formed over the whole concentration range while the intermediate compositions of TiO$_2$–SnO$_2$ are difficult to obtain because of the miscibility gap. The fundamental absorption edge shows a systematic positive displacement (towards higher photon energies) for amorphous samples of SrTiO$_3$–BaTiO$_3$ with the increased atomic ratio of Ba/(Sr+Ba). The opposite shift in the absorption spectra near the band gap is observed for polycrystalline samples. This effect should be discussed in terms of the modification of the local environment of Ti ion and distortion of Ti–O bond length. Such experimental evidence can be provided only by EXAFS/XANES techniques.

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