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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 ($2\theta = 0.02$ 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

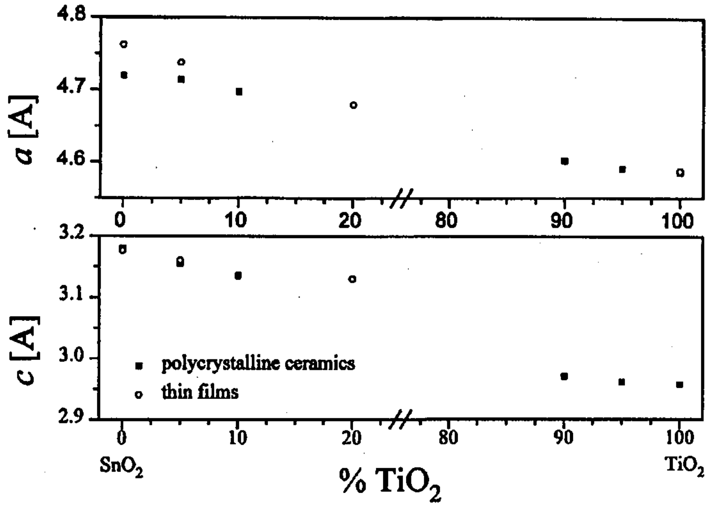

Fig. 1. The lattice parameters a and c of the tetragonal rutile as a function of TiO_2 content in TiO_2-SnO_2 solid-state solutions. The preferential growth of Ti-rich TiO_2-SnO_2 thin films makes it impossible to determine c.

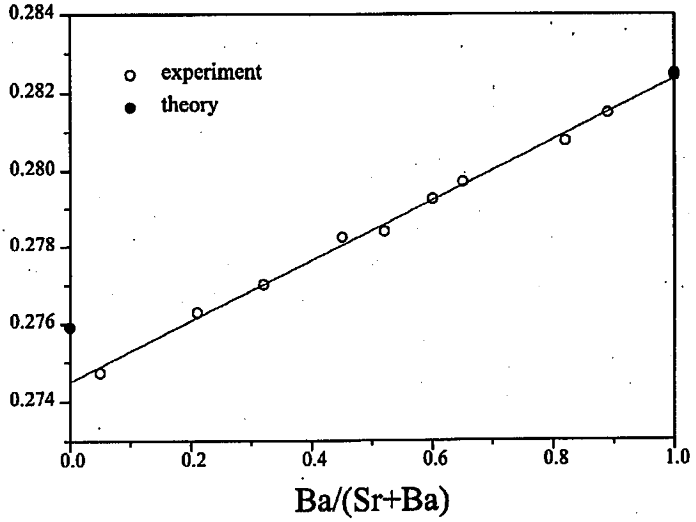

Fig. 2. The interplanar spacing d_{hkl} as a function of Ba/(Sr+Ba) atomic ratio in $SrTiO_3$-$BaTiO_3$ thin films after annealing.

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,

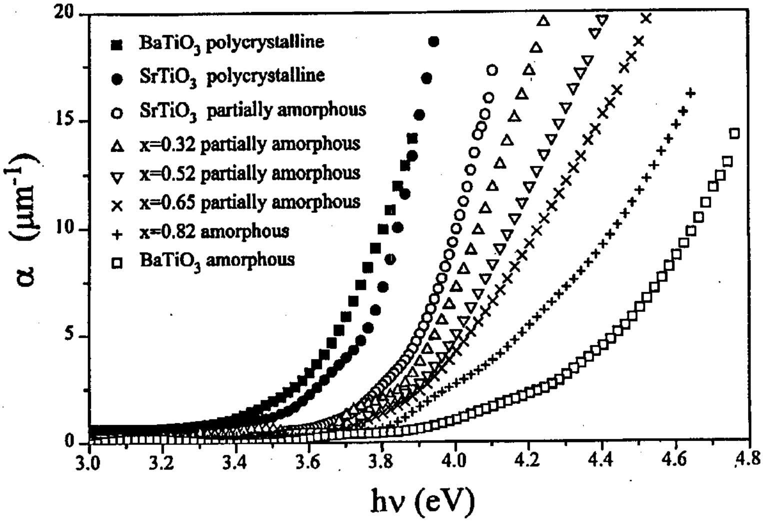

Fig. 3. Spectral dependence of the absorption coefficient α for amorphous and polycrystalline thin films of $SrTiO_3$–$BaTiO_3$.

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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