JOURNAL OF MATERIALS SCIENCE 22 (1987) 1240–1242

An effect of heat treatment on the real structure of components of $ZnO–SnO_2$ mixtures

P. LOŠŤÁK, M. PŘEDOTA, L. BENEŠ, J. HORÁK
University of Chemical Technology, Leninovo nám.565, 532 10 Pardubice, Czechoslovakia
V. RAMBOUSEK
VÚEK, Pospíšilova 281, 500 64 Hradec Králové, Czechoslovakia

The effect of heat treatment (24 h at 500° C) on the structure and properties of $ZnO–SnO_2$ mixture with 0 to 10 mol % SnO_2 was studied. An increase in the SnO_2 content results in a decrease of the lattice parameters of ZnO, an increase of electrical conductivity and a decrease of the intensity of green luminiscence in the heat-treated $ZnO–SnO_2$ samples. These results are explained in terms of the interaction of interstitial $Zn_i^{\cdot}$ and $Zn_i^{\cdot\cdot}$ atoms with oxygen atoms from the SnO_2 layer formed on ZnO grains, which results in a decrease of ZnO lattice parameters. Simultaneously, oxygen atoms from SnO_2 occupy uncharged oxygen vacancies in ZnO, thus decreasing its green luminiscence. The described interaction is supposed to result in the formation of amorphous SnO_{2-x} on the surface of ZnO crystallites.

1. Introduction

The reaction of ZnO with SnO_2 at temperatures above 900° C results in the formation of Zn_2SnO_4 [1]. According to Filippova *et al.* [2] the heating of ZnO with SnO_2 in the molar ratio 2 : 1 for at least 8 h at 1200° C results in the formation of Zn_2SnO_4 with a yield of 96.8%. But there are no data in the literature on a possible interaction of these oxides at substantially lower temperatures.

In the present paper we report the study of the interaction of ZnO with SnO_2 at the temperature of 500° C. A study of the effect of this heat treatment on the structure, electric conductivity and the luminiscent properties of the $ZnO–SnO_2$ mixtures had the aim of detecting a possible interaction of the components and changes in the real structure of these components.

2. Experimental procedure

2.1. Preparation of ZnO

As a starting material for the preparation of "pure" ZnO we have used metallic zinc of 5N purity, HNO_3 of the purity used for semiconductors and an ammonium solution prepared by the absorption of gaseous NH_3 in redistilled water.

The metallic zinc was dissolved in hot nitric acid. After cooling the obtained solution to the room temperature, $Zn(OH)_2$ was precipitated by the addition of ammonium solution. The obtained zinc hydroxide was separated by filtration and after drying was decomposed to ZnO by heating in platinum crucible at 500° C for 24 h.

2.2. Preparation of $ZnO–SnO_2$ mixtures

In order to obtain perfectly homogeneous mixtures of $ZnO–SnO_2$, the samples were prepared using the following technique: metallic tin of 5N purity was dissolved in hot concentrated HNO_3 and the obtained solution was evaporated to a small volume, diluted with redistilled water and then a corresponding amount of solid ZnO was added to this solution. The obtained solution was thoroughly mixed, water was carefully evaporated and the dry residue was heat-treated in a platinum crucible at 500° C for 24 h.

This procedure was used for the preparation of $ZnO + xSnO_2$ samples with $x = 0.1, 0.3, 0.5, 1.0, 5.0$ and 10.0 mol %.

2.3. Determination of lattice parameters

X-ray powder diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (VEB Freiberger Präzisionsmechanik, GDR), equipped with a goniometer of 25 cm diameter and a proportional detector. $CuK\alpha$ radiation was used with the elimination of K_β radiation by a nickel filter; in the range $2\theta = 10$ to 35° the interplanar spacing was calculated using $CuK\alpha$ radiation ($\lambda = 0.154\,178$ nm) and in the range $2\theta = 35$ to 90° $CuK\alpha_1$ radiation ($\lambda = 0.154\,051$ nm) was used.

Powdered silicon ($a = 0.543\,055$ nm) served as an internal standard. The lattice parameters were computed using the least-squares technique to increase the accuracy, the minimized quantity being $(2\theta_{exp} - 2\theta_{calc})^2$.

2.4. Determination of the high-frequency electrical conductivity

As the d.c. measurement of electrical conductivity is associated with experimental difficulties, we have used the determination of high-frequency electrical conductivity for a comparison of the electrical properties of powder samples. The quality factor was determined for an oscillator circuit composed of the self-inductance and the measuring capacitor, whose dielectric was made of the investigated oxide mixture in the

0022–2461/87 $03.00 + .12

TABLE I Lattice parameters of samples of the $ZnO-SnO_2$ system

Sample	a(nm)	c(nm)	V(nm^3)	Δ*
ZnO	0.32499(2)	0.52068(5)	0.047625(9)	0.004
ZnO + 0.1 mol % SnO_2	0.32497(1)	0.52065(2)	0.047617(3)	0.004
ZnO + 0.3 mol % SnO_2	0.32495(2)	0.52060(2)	0.047607(5)	0.003
ZnO + 0.5 mol % SnO_2	0.32495(1)	0.52059(1)	0.047606(3)	0.004
ZnO + 1.0 mol % SnO_2	0.32494(2)	0.52059(3)	0.047602(9)	0.003
ZnO + 5.0 mol % SnO_2	0.32495(1)	0.52057(1)	0.047603(3)	0.003
ZnO + 10.0 mol % SnO_2	0.32493(1)	0.52052(2)	0.047594(4)	0.004

*$\Delta = 1/N \sum_1^N |2\theta_{exp} - 2\theta_{calc}|$, where $2\theta_{exp}$ is the experimental diffraction angle, $2\theta_{calc}$ is the angle calculated from lattice parameters and N is the number of investigated diffraction lines.

form of a tablet of diameter 13 mm and thickness 2 mm. Using the values of the quality factor Q_1 and the capacitance C_1 of the condensor with air as the dielectric (empty capacitor) and the quality factor Q_2 of the capacitor filled with the sample, the real part of the high-frequency electrical conductivity G_{px} was calculated from the relation

$$G_{px} = \frac{Q_1 - Q_2}{Q_1 Q_2} \omega C_1 \quad (1)$$

using the measuring frequency $f = 18$ MHz ($\omega = 2\pi f$).

2.5. Measurement of luminiscence spectra

The luminiscence of the studied samples was measured using a Hitachi Perkin-Elmer MPF-2A fluorescence spectrometer. Interference filter 333 and UV filter D25 were used in the excitation part and filter 35 was used in the emission part. The relative intensity was measured in comparison with the standard NBI/SO1.

3. Results

X-ray diffraction analysis of the $ZnO-x\ SnO_2$ samples with $x = 0.0$ to 10.0 mol % SnO_2 revealed only the diffraction lines of the hexagonal wurtzite structure of ZnO. The diffraction lines of SnO_2 have not been found even in the $ZnO-SnO_2$ sample containing 10.0 mol % SnO_2. The lattice parameters a and c and the volume of the elementary unit cell V of the prepared samples are summarized in Table I. As can be seen from Fig. 1, all the above parameters decrease at first abruptly in the region of $x = 0.0$ to 1.0 mol % and then slowly in the region of 1.0 to 10.0 mol % SnO_2.

The values of the high-frequency dielectric constant G_{px} of $ZnO-SnO_2$ samples are presented in Table II. As can be seen from Fig. 2, G_{px} increases with increasing content of SnO_2 in the samples.

Luminiscence spectra of the prepared samples are shown in Fig. 3. As can be seen from this figure, with increasing SnO_2 content the green luminiscence of the starting ZnO decreases.

TABLE II Real part of h.f. electrical conductivity of samples of the $ZnO-SnO_2$ system

Sample	G_{px}($10^{-6}\Omega^{-1}$)
ZnO	1.89
ZnO + 0.1 mol % SnO_2	2.38
ZnO + 0.3 mol % SnO_2	7.52
ZnO + 0.5 mol % SnO_2	5.69
ZnO + 1.0 mol % SnO_2	12.57
ZnO + 5.0 mol % SnO_2	11.20
ZnO + 10.0 mol % SnO_2	19.37

4. Discussion

According to the X-ray diffraction analysis, $ZnO-SnO_2$ mixtures prepared by the above procedure reveal only one crystalline phase with the diffraction lines of ZnO. Even on the diffraction diagram of the sample containing 10 mol % SnO_2 we have not found the diffraction lines of SnO_2 or the compound Zn_2SnO_4 resulting from the reaction of ZnO with SnO_2 at high temperatures [1, 2]. For a comparison we have prepared pure SnO_2 by the same procedure, i.e. by the dissolution of tin in HNO_3 followed by the decomposition of the obtained product under the same conditions as the studied samples. In this case the X-ray diffraction revealed the presence of tetragonal SnO_2 crystals.

Because some literature data [3–5] describe the formation of amorphous SnO_2 under various preparation conditions, we assume that in our case also the absence of SnO_2 diffraction lines in the X-ray diffractograms of $ZnO-SnO_2$ mixtures can be explained by the formation of an amorphous SnO_2 phase.

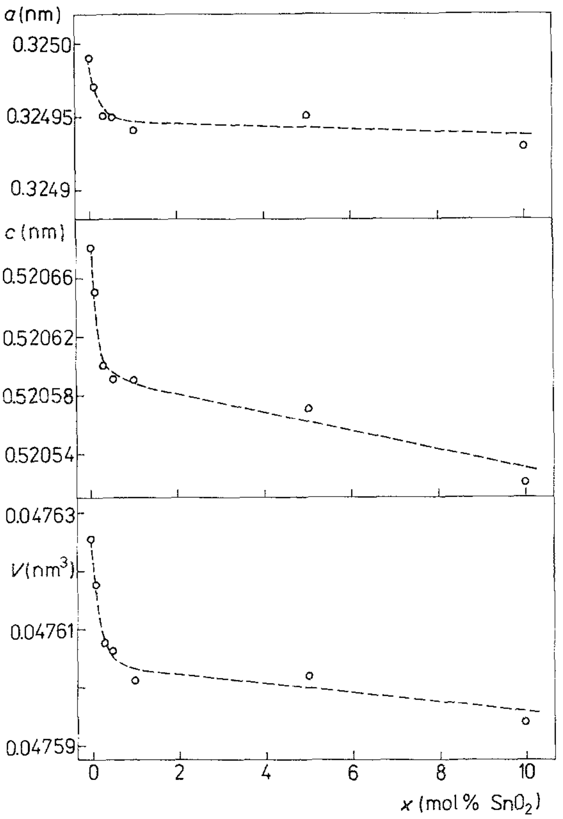

Figure 1 The dependence of lattice parameters a and c and the volume V of the elementary unit cell of ZnO on the content of SnO_2 in $ZnO-SnO_2$ powder samples.

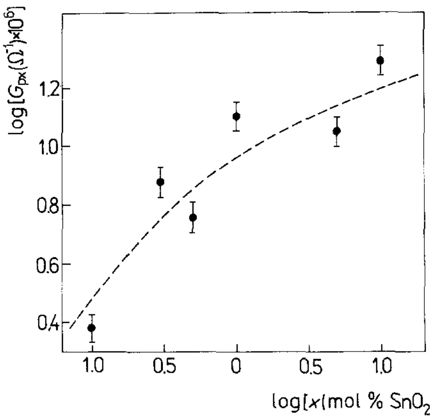

Figure 2 The dependence of high-frequency electrical conductivity G_{px} of $ZnO-SnO_2$ mixtures on the SnO_2 content.

During the thermal decomposition of the suspension of ZnO in hydrated tin (IV) oxide solution, an amorphous layer of SnO_2 phase is formed on the surface of ZnO particles. During the following heat treatment at 500° C we can suppose that the interaction of ZnO with SnO_2 takes place. This interaction is manifested by the decrease of the lattice parameters and the volume of elementary unit cell of ZnO (see Fig. 1).

The observed decrease in the lattice parameters can be explained by the interaction of oxygen atoms from the SnO_2 layer with interstitial $Zn_i^{\cdot}$ or $Zn_i^{\cdot\cdot}$ atoms present inside the ZnO lattice. This interaction leads to the diffusion of zinc interstitials towards the surface of particles where new layers of ZnO wurtzite modification grow. As the concentration of zinc interstitials is relatively low, a small concentration of SnO_2 is sufficient for the realization of this process which takes place on the boundary between the both phases. Therefore, the observed abrupt decrease in the volume of the elementary unit cell takes place in the region of small concentrations of SnO_2.

A decrease in the content of interstitial $Zn_i^{\cdot}$ and $Zn_i^{\cdot\cdot}$ atoms should result in a decrease in the concentration of free electrons in ZnO and thus in a decrease in the electrical conductivity of the samples. The change of the high-frequency dielectric conductivity G_{px} with increasing SnO_2 content shows an opposite behaviour (see Fig. 2), i.e. the electrical conductivity increases with increasing SnO_2 content. We assume that the observed increase of the electrical conductivity can be ascribed to the non-stoichiometry of the SnO_2 layer deposited on the ZnO surface, because the release of oxygen from the SnO_2 lattice results in an increase in the concentration of free electrons [6–8].

The suggested explanation of the obtained experimental data was compared with the results of Paria and Marti [9], who studied point defects in SnO. On the basis of their study of conductivity changes in SnO_2 they assume the presence of vacancies $V_O^{\cdot}$ and anti-Frenkel defects ($O^{\cdot}$ interstitials) in the SnO_2 lattice. This conclusion is in good agreement with our results, because interstitial oxygen atoms will be more favoured for the proposed reaction with $Zn_i^{\cdot}$ interstitials than oxygen atoms in the lattice sites of SnO_2.

We assume that the SnO_2 layer on the surface of ZnO crystallites releases oxygen. The oxygen atoms from SnO_2 react not only with interstitial zinc atoms, but we cannot exclude that some of these oxygen atoms can occupy oxygen vacancies in the ZnO crystal lattice. This supposition is supported by changes in the luminiscence spectra. According to the literature data, the green luminiscence of ZnO is associated with the presence of uncharged oxygen vacancies [10–12]. From Fig. 3 we can see that the luminiscence in the green region decreases with increasing SnO_2 content, which is in agreement with the above suggested interaction. Therefore, we can conclude that the net change in the electrical conductivity of $ZnO-SnO_2$ mixtures with increasing SnO_2 content is effected mainly by the increase in the concentration of free carriers in the SnO_{2-x} layer caused by the interaction with ZnO.

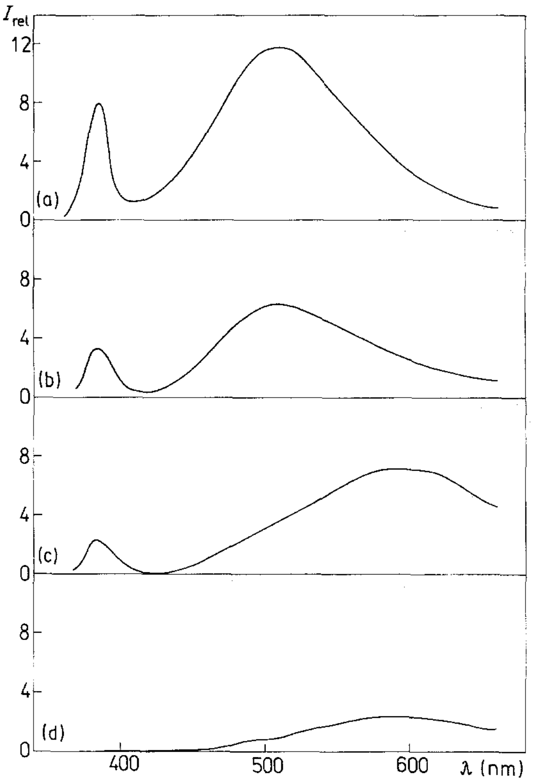

Figure 3 Luminiscence spectra of $ZnO-SnO_2$ mixtures with various contents of SnO_2: (a) 0.1, (b) 0.3, (c) 1 and (d) 10 mol % SnO_2.

References

1. H. TAZAKI and S. KUWABARA, *J. Sci. Hiroshima Univ. A* **15** (1952) 263.
2. N. A. FILIPPOVA, E. V. SAVINA and V. A. KOROSTELOVA, *Zh. Neorg. Khim.* **5** (1960) 1423.
3. K. H. SUN, *Glass Ind.* **27** (1946) 552.
4. G. S. COLLINS, T. KACHNOWSKI and N. BENCZER-KOLLER, *Phys. Rev. B* **19** (1978) 1369.
5. G. KELLY, *Nucl. Instrum. Meth. Phys. Res.* (1983) 209.
6. B. P. KRYZHANOVSKII, *Zh. Tekh. Fiz.* **28** (1958) 1489.
7. H. J. VAN DAAL, *Solid State Commun.* **6** (1968) 5.
8. A. F. PETERSON, Dissertation, Rutgers State University (1968); *Diss. Abstr. B* **29** (1968) 1342.
9. M. K. PARIA and H. S. MARTI, *J. Mater. Sci.* **18** (1983) 2101.
10. F. A. KRÖGER and H. I. VINK, *J. Chem. Phys.* **22** (1954) 250.
11. E. MOLLWO, *Z. Phys.* **162** 557.
12. P. H. KASAI, *Phys. Rev.* **130** (1963) 989.

Received 15 May
and accepted 23 July 1986