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Interaction of zinc oxide with bismuth oxide

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The lattice parameters of polycrystalline ZnO in mixtures of ZnO–Bi_2O_3 and their dependence on Bi_2O_3-concentration were determined. Simultaneously the influence of ZnO presence on the origin of various modifications of Bi_2O_3 was observed. On the grounds of the measured decrease of the elementary cell volume the supposition about the interaction of Zn-intersititals with overstoichiometric oxygen atoms in Bi_2O_3 was accepted. In accordance with this idea the changes of free carrier concentration of samples ZnO + 5 mol% Bi_2O_3 in the dependence on annealing temperature were found.

1. Introduction

No new compounds have been identified on interaction between ZnO and Bi_2O_3; the phase diagram [1] revealed the existence of an eutectic corresponding to ZnO · 24 Bi_2O_3 composition. Also, any building-in of bismuth atoms into the crystal lattice of ZnO has not been reported either; the existence of interstitials or substitutional defects does not seem probable in view of the size of the bismuth atom. So far, the interaction of the oxides in question has not been systematically studied with regard to possible changes in the physical properties of zinc oxide. Nevertheless, it has been shown in [2] that some properties of the ZnO–Bi_2O_3 samples are affected by changing the modification of Bi_2O_3.

In the present paper we report the results of measurements of the changes in the lattice parameters of ZnO samples after heat treating the ZnO–Bi_2O_3 mixtures with different bismuth oxide contents, and the electrical conductivity of these polycrystalline samples prepared at different temperatures. Our objective is to show that heat treatment of polycrystalline ZnO–Bi_2O_3 samples leads to changes in the real structure of the interacting substances.

2. Experimental details

2.1. Preparation of ZnO samples with Bi_2O_3 admixture

As a starting material for the preparation of the ZnO–Bi_2O_3 mixed oxide samples we used ZnO p.a. whose purity was verified by means of emission spectral analysis; trace quantities of aluminium, iron, lead, silicon, copper, cadmium and silver were found. The bismuth oxide was prepared from elemental bismuth of 5 N purity by dissolving it in concentrated HNO_3 p.a. at elevated temperature. After thickening of the solution, the crystallized $Bi(NO_3)_3$ was isolated by filtration.

In order to attain perfect homogeneity of the ZnO–Bi_2O_3 samples, they were prepared using a wet technique as follows: a calculated quantity of $Bi(NO_3)_3$ was dissolved in redistilled water and the corresponding charge of ZnO was added to the solution. The suspension thus formed was thoroughly mixed, carefully dried and the solid phase was then introduced into a nickel crucible where it was annealed at a given temperature for 24 h.

Two sets of samples were prepared in this way:

(a) samples annealed at 500° C whose composition was ZnO + x Bi_2O_3 $x = 2, 5, 10, 15, 20$ and 25 mol %;

(b) samples of composition ZnO + 5 mol % Bi_2O_3 annealed at 400, 500, 600, 700 and 800° C.

2.2. Determination of lattice parameters

The X-ray powder diffractograms of the samples were measured using a vertical X-ray diffractometer HZG-4 (VEB Freiberger Präzisionsmechanik, GDR) equipped with a goniometer of 25 cm diameter, in the 10 to 90° 2θ range. Cu$K\alpha$ ($\lambda = 0.154\,178$ nm) radiation was used for the angular range of $2\theta < 35°$ and $K\alpha_1$ ($\lambda = 0.154\,051$ nm) for the range of $2\theta > 35°$, employing a nickel filter for attenuation of the $K\beta$ radiation. A proportional detector 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 improve the accuracy, the minimized quantity being $(2\theta_{\text{exp}} - 2\theta_{\text{calc}})^2$.

2.3. Determination of the high-frequency electrical conductivity

In view of the fact that the measurements of the electrical conductivity of powdered materials by means of a d.c. method are difficult and that the preparation of the samples by pressing or, eventually, by further heat treatment changes considerably their basic physical parameters, we adopted the determination of the high-frequency electrical conductivity in order to compare the properties of the ZnO–Bi_2O_3 samples. The method consisted of determining the quality factor of the oscillator circuit formed by the self-inductance and by the capacitance of a measuring capacitor whose dielectric was made of the investigated oxide mixture sample. Using the values of the

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TABLE I

Sample	ZnO			Bi_2O_3				
	a (nm)	c (nm)	$\Delta 2\theta$[a]	a (nm)	b (nm)	c (nm)	β (deg)	$\Delta 2\theta$[a]
ZnO	0.324 99(3)	0.520 68(5)	0.005	–	–	–	–	–
ZnO + 2% Bi_2O_3	0.325 00(3)	0.520 60(4)	0.004	1.094 64(9)[b]	–	0.563 67(8)	–	0.005
ZnO + 5% Bi_2O_3	0.324 99(3)	0.520 61(4)	0.004	1.094 90(8)[b]	–	0.563 32(7)	–	0.005
ZnO + 10% Bi_2O_3	0.324 97(3)	0.520 61(3)	0.004	1.094 92(6)[b]	–	0.563 39(4)	–	0.005
ZnO + 15% Bi_2O_3	0.324 99(3)	0.520 53(8)	0.005	1.094 97(8)[b]	–	0.563 34(9)	–	0.005
ZnO + 20% Bi_2O_3	0.324 98(2)	0.520 56(5)	0.005	1.0223(2)[c]	–	–	–	0.012
ZnO + 25% Bi_2O_3	0.325 01(2)	0.520 51(9)	0.007	0.5851(1)[d]	0.8165(1)	0.7510(1)	67.073(4)	0.008
Bi_2O_3	–	–	–	0.5850(1)[d]	0.8167(1)	0.7505(1)	67.073(7)	0.014

[a] $\Delta 2\theta = \frac{1}{N}\sum_{1}^{N} |2\theta_{obs} - 2\theta_{calc}|$.

[b] Tetragonal, space-group $C\bar{4}2b$.

[c] Cubic, space-group I23.

[d] Monoclinic, space-group P2*q*/*c*.

quality factor Q_1 and capacitance C_1 of the capacitor with air as the dielectric and the values Q_2 and C_2 corresponding to the capacitor filled with the sample, we calculated the real part of the high frequency electrical conductivity according to the relation

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

The measurements were carried out at a frequency $\omega = 2\pi f$ ($f = 18$ MHz).

3. Results

The set of ZnO–Bi_2O_3 samples prepared at 500° C was investigated using X-ray powder diffraction. The obtained values of the lattice parameters of hexagonal ZnO and Bi_2O_3 present in individual samples in different modifications are summarized in Table I. The dependence of the elementary cell volume, calculated from the corresponding parameters of zinc oxide, on the Bi_2O_3 concentration in the mixture is shown in Fig. 1. Table II summarizes the results of the measurements of the high-frequency electrical conductivity (i.e. the values of G_{px} and Q_2) of the ZnO + 5 mol% Bi_2O_3 samples prepared at different temperatures. The temperature dependence of these parameters is shown in Fig. 2.

4. Discussion

As the experimental results indicate, a solid Bi_2O_3 phase is formed on the surface of polycrystalline ZnO by decomposition of $Bi(NO_3)_3$ at temperatures of about 500° C. From the literature data on the stability of individual modifications of Bi_2O_3 [3] one can expect that at the mentioned temperature the monoclinic modification of Bi_2O_3 is formed. Our experiments have shown, however, that in the given temperature interval layers of tetragonal β-modification of Bi_2O_3 grow on the surface of ZnO crystalline grains in the ZnO–Bi_2O_3 mixtures containing up to 15 mol% Bi_2O_3 (Table I). Only after increasing the concentration in excess of 15 mol% Bi_2O_3 starts to appear the cubic γ-modification corresponding to I23 space group and characterized by the lattice constant $a = 1.0223$ nm, whereas the monoclinic α-modification of Bi_2O_3 has been identified on further increasing the bismuth oxide concentration in the ZnO–Bi_2O_3 system in the range above 25 mol% Bi_2O_3.

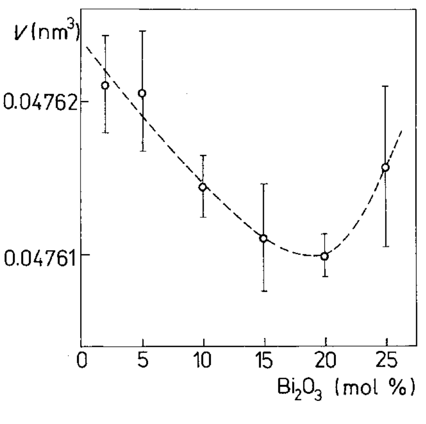

Figure 1 Cell volume against Bi_2O_3 content.

The anomalous formation of the tetragonal β-modification of Bi_2O_3 on the surface of the ZnO crystal grains is most probably due to the structure of the substrate on which the bismuth oxide layer grows. The formation of β-Bi_2O_3 layers on the ZnO crystal faces should be therefore understood as a result of the epitaxial growth coming into force after the decomposition of $Bi(NO_3)_3$.

The deposition of bismuth oxide layers on the ZnO crystals also gives rise to a change in the physical properties of zinc oxide. Bi_2O_3 is known only as an oxide with hole conductivity, which is due to excess oxygen in the lattice, whereas polycrystalline ZnO used in our experiments always exhibited a high electron conductivity, due to the existence of interstitial $Zn_i^{\cdot}$ in the ZnO wurtzite lattice. On thermal treatment of the ZnO–Bi_2O_3 samples one can assume the $Zn_i^{\cdot}$

TABLE II

Sample	Annealing temperature (K)	Q_2	G_{px}/G_{px_0}*
ZnO + 5 mol% Bi_2O_3	683	120.0	4.69
	793	163.6	1.08
	893	172.5	0.84
	968	114.0	5.38
	1073	107.0	10.60

*G_{px_0} is related to pure ZnO ($G_{px_0} = 2.49 \times 10^{-6}\,\Omega^{-1}$).

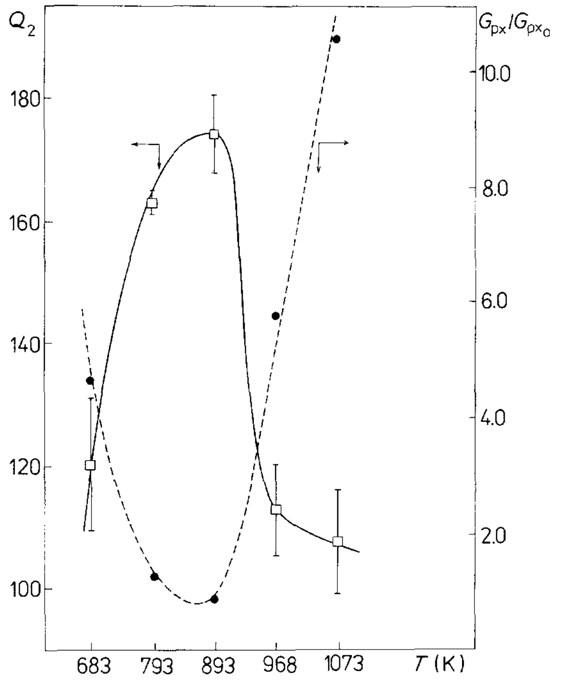

Figure 2 Electrical conductivity against temperature.

interstitials interact with excess oxygen atoms of the Bi_2O_3 lattice. Such an interaction would necessarily lead to a lowering of the concentration of $Zn_i^{\cdot}$ interstitials, hence also to a lowering of the free electron concentration in the wurtzite phase of ZnO. At the same time, the concentration of bismuth vacancies in the interface region of the $ZnO-Bi_2O_3$ phases would be suppressed too, which would result in a lowering of the concentration of free holes. This idea is supported by the observed decrease of the high-frequency electrical conductivity of the $ZnO-Bi_2O_3$ system with increasing annealing temperature of $Zn_i^{\cdot}$ interstitials into the boundary region between the two phases is rather weak at low temperatures whereas this process becomes more favoured on increasing the temperature, which leads at a certain temperature to maximum suppression of the point defects that give rise to free carriers in both phases. That is why a minimum in the electrical conductivity is observed in the plot of Fig. 2. Further, an increase in the annealing temperature of the samples results in an increase in the value of G_{px}. This increase of the electrical conductivity is apparently due to incorporation of the oxygen from the gas phase into the thin layers of Bi_2O_3 that fill the space among individual grains of polycrystalline ZnO. This view is confirmed by a markedly lower value of the quantity G_{px}, found on measuring the samples annealed in an inert atmosphere.

Indirect proof of the essential correctness of the above mentioned ideas is provided by the measurements of the changes in the lattice parameters of zinc oxide and its elementary cell volume, shown in Fig. 1.

The value of the lattice parameter c, determined for a set of $ZnO-Bi_2O_3$ samples subjected to identical heat treatment, decreases on increasing the concentration of Bi_2O_3; the same applies to the volume of the elementary cell of ZnO. In our opinion, this phenomenon is due to diffusion of the $Zn_i^{\cdot}$ interstitials from the crystal lattices towards the surface where interaction with superstoichiometric oxygen atoms and/or bismuth vacancies takes place.

One can thus assert that on interaction of polycrystalline oxides ZnO and Bi_2O_3 the real structure of both ZnO and Bi_2O_3 becomes modified in the contact regions between both phases; the surface layers of the ZnO phase become depleted in the $Zn_i^{\cdot}$ interstitials whereas a decrease in the concentration of bismuth vacancies takes place in the Bi_2O_3 layers growing on the ZnO crystal grains.

5. Conclusions

Interaction of polycrystalline ZnO with Bi_2O_3 at elevated temperatures leads to a decrease in the value of the lattice parameter c and of the elementary cell volume of ZnO with growing concentration of Bi_2O_3 in the mixture. On explaining this effect by the notion of the disappearance of $Zn_i^{\cdot}$ particles from the interstitial sites we come to the conclusion that the lowest values of the c parameter and the lowest values of the volume of the elementary cell are probably closest to the true value of the lattice parameters (and the volume of elementary cell) of pure, unperturbed zinc oxide, i.e. ZnO free of interstitials. In agreement with this conclusion, the observed values of the lattice parameters of zinc oxide lie at the lower limit of the published data [4, 5]. The observed ratio $c/a = 1.6015$ [5] is in good agreement with the literature data given in [6], being slightly lower than the values quoted in [4].

It is therefore suggested that the annealing of polycrystalline ZnO particles surrounded by a layer of Bi_2O_3 concentration, etc. creates the conditions under which one can prepare wurtzite modification of ZnO containing a minimum of interstitials.

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