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Analytical Note

Quantification of modifiers in advanced materials based on zinc oxide by total reflection X-ray fluorescence and inductively coupled plasma mass spectrometry

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ABSTRACT

A novel approach to quantification of Ga and Zn modifiers in advanced materials based on zinc oxide is presented. The approach includes a combination of total reflection X-ray fluorescence (TXRF) and inductively coupled plasma mass spectrometry (ICP-MS) for determination and validation of the results. It is suggested to use aqueous standards for the direct determination of elements in powder samples by TXRF with a relative standard deviation no more than $s_r = 0.11$. The accuracy of these results was proved by ICP-MS after the sample decomposition, $s_r(\text{In}) = 0.05$, $s_r(\text{Ga}) = 0.06$ and $s_r(\text{Zn}) = 0.06$. It was established that there is a possibility to determine indium above 300 ppb on the background of K-M3 line of argon.

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1. Introduction

Zinc oxide can be used in parts of solar batteries, piezoelectric transducers, as sensitive materials for gas sensors as well as for transparent electrodes. However, zinc oxide is a highly resistive material and it complicates the correct measurement of its electric characteristics and limits its application in transparent electrodes and gas sensors. One of the ways to increase ZnO conductivity is to dope it by donor impurities, including elements of the third group — Al, Ga, and In. Nowadays, chemical methods for the synthesis from the liquid phase are actively used for receiving functional materials based on zinc oxide. The distinct feature of these methods is a great difference in quantity of components in the final product and quantity of the precursor. In this regard, the investigation of methods for determining the composition of the materials obtained in various ways is of exceptional importance for the establishment of the relationship "the conditions of synthesis — functional properties." At the same time, one of the problems is the absence of standard reference materials for advanced samples. Nanocomposites based on zinc oxide are high dispersive powders with the crystal grains of 15–30 nm, with a total content of doping impurities from 0.1% to 3%. Currently methods of a surface analysis of solid samples and their solutions are commonly used to quantify the doping impurities. It should be noted that the results of quantification are usually compared by different analytical techniques because of the absence of standard reference materials for advanced samples [1–3].

The advantage of total reflection X-ray fluorescence (TXRF) method is a direct non-destructive analysis. Its sensitivity is sufficient to determine the modifiers in samples of different composition at a level of 0.1%, but the accuracy of the results depends on the sample preparation [4]. To reduce the influence of loss and contamination caused by the procedure of the sample preparation we should analyze advanced materials directly in powder samples. However, in this case, the results depend on the homogeneity of the matrix composition, the reproducibility of powder sampling on the carrier, the surface morphology, the sample weight and the calibration method [5]. Gallium is determined by TXRF in solutions of different compositions [6] and in suspensions of soil [7]. Gallium is often used as an internal standard for quantitative calculations [8]. During the determination of indium by TXRF overlapping of K-M_3 line of argon (3.2 keV) with L_3-M_5 line of In (3.3 keV) is possible, that is why the optimization of the experimental conditions is aimed to reduce this spectral interference is required. It should be noted that the determination of indium by TXRF is insufficiently described in literature because argon can influence the results of the analysis. A method for the elimination of the influence of argon on the determination of some elements has been suggested. To achieve this result the purge chamber with nitrogen was used [9]. Moreover, TXRF conditions were modified to excite In K-L_3 (24.2 keV) using a continuous X-ray radiation strip (28–35 keV) [10].

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Methods for the determination of indium and gallium by inductively coupled plasma mass spectrometry (ICP-MS) are widely used for determination of the wide range of the elements in different samples [11] The limits of detection of In and Ga by ICP-MS are rather low and both analytes are free from polyatomic interference in the zinc oxide solutions. It makes possible to use ICP-MS as the reference analytical technique of to validate the results obtained by TXRF method when the standard reference samples are absent. In present work, the novel approach to quantify the modifiers of Ga and In in the materials on the basis of zinc oxide by TXRF with the validation of the results by ICP-MS

2. Materials and methods

2.1. Synthesis of materials

Nanocrystalline ZnO (Ga, In) powders were synthesized by the coprecipitation method. To obtain the precursors' mixtures with different contents of metal cations the aqueous solutions of Zn $(NO_3)_2$ (1.2 M), Ga $(NO_3)_3$ (0.2 M) and In $(NO_3)_3$ (0.2 M) were mixed. Gallium content in the solutions of precursors' mixtures was 1 at.% [Ga]/([Ga] + [Zn]), but indium content was varied in the range of 0–10 at.% [In]/([Ga] + [In] + [Zn]). The total quantity of Mn + (M = Zn, Ga, In) in the precursors' mixtures was 0.25 mol. The solution containing zinc, gallium and indium nitrates was slowly added to a stirred solution of NH_4HCO_3 (1.9 M) at 60 °C. After aging for 1 h at room temperature the precipitate (white powder) was centrifuged, washed five times with deionized water to remove residual ions, dried at 50 °C for 24 h and annealed at 250 °C for 24 h. Phase composition and crystal structure were determined by X-ray diffraction (Rigaku diffractometer, monochromatized Cu K-L_3 radiation). All samples annealed at 250 °C included nanocrystalline ZnO (wurtzite). Gallium or indium containing phases were not detected. This may be caused by the lack of sensitivity of this method of the determination or by receiving X-ray amorphous phases in the process of synthesis.

2.2. Analytical procedures

2.2.1. ICP-MS

Measurements were performed using a mass spectrometer with inductively coupled plasma Agilent 7500C (Japan), quadruple mass analyzer. The device was controlled via the PC software ChemStation (version G1834B) software package (Agilent Technologies). To prepare working and standard solutions concentrated nitric acid (65%) of the grade «Suprapure» (Merck, Germany) and deionized water Millipore Simplicity (Millipore, France) (18.2 mΩ/cm) were used. To prepare the standard solutions and a model mixture monoelement Zn, Ga and In a concentration of 10 mg/L (High Purity Standards, USA) were used. Following isotopes were used 66Zn, 67Zn, 68Zn, 71Ga, and 115In.

2.2.2. Preparation of solutions of powder samples based on ZnO composition $ZnGaIn_x$

To determine the content of Ga and In in powder samples the samples of 0.0020 g were weight in a vial and dissolution by nitric acid (1:1). After sample dissolution, the received solution was adjusted to a volume of 2 ml with deionized water. Further, the stock solution was diluted 1000-fold in a 10 ml vial using a manual sampler. To avoid contamination of the sample input's system and of ion optics the range of operating concentrations was chosen so that the zinc content in the sample solution was not above than 1000 ppb. Thus the concentrations of indium and gallium were 20–200 ppb and 5–20 ppb respectively.

2.2.3. TXRF

Measurements were performed on a spectrometer TXRF S2 PICOFOX (Bruker Nano GmbH, Germany). Mo K-L3 was used for excitation of the X-ray fluorescence. The spectrum acquisition time was 250 s. In order to establish the range of linear dependence of the analytical signal model solutions of Ga, Zn, and In were prepared and their concentrations were between 100 and 1000 ppb. 3 μL of the solution was applied on a quartz reflector with a dispenser. After pre-drying the dry residue was analyzed by TXRF sample using quartz reflectors. Firstly, the reflector was treated in 10% nitric acid solution for a few hours. Then to check the purity of the reflector the determination of impurities was made. Before each subsequent measurement the reflector was washed with acid, water and acetone. To determine Ga and In in $ZnGaIn_x$ powder composition samples were applied to a reflector by petrolatum lubrication.

3. Results and discussion

To evaluate the possible polyatomic interferences in the determination of gallium and indium under conditions of the overage of zinc the model mixture was prepared. The approximate content of components in the analyzed materials was taken into account. To characterize the composition of new materials the ratio of cations in atomic percents is most preferred. An important feature of nanocrystalline zinc oxide is a deviation of its composition from stoichiometric composition of the components during the synthesis. ZnO phase always exists with oxygen deficiency, and δ in $Zn_{1+\delta}O$ is about $5.9 \cdot 10^{-6}$ and $1.5 \cdot 10^{-4}$ at synthesis temperature of 700 and 1100°C, respectively. Moreover, for nanocrystalline systems the oxygen adsorption on the oxide surface becomes significant [12], which causes the uncertainty of Zn/O ratio. Therefore, the most informative method for presenting content of additives in zinc oxide is the ratio Ga/Zn or In/Zn, which does not depend on the oxygen concentration in the sample. Taking into account considerable differences in the masses of the elements, the representation of the analysis as a ratio of the content of metals in the form of atomic percent is preferred because it allows comparing the influence of the same amounts of various impurities on the functional properties of zinc oxide. According to the obtained results (Table 1), there is a possibility to determine In, Ga and Zn in powder samples based on zinc oxide after dissolution with a relative standard deviation $s_r(In) = 0.05$, $s_r(Ga) = 0.06$ and $s_r(Zn) = 0.06$.

As a rule, to analyze the powder samples by TXRF using the internal standard slurries are prepared. At the same time, to achieve the aggregate and sedimentation stability of the resulting systems the stabilizing agent is needed. To select a stabilizing agent it is necessary to make additional researches for each specific material. We suggest the element of the sample — zinc — as an internal standard for accounting various effects on the results of the determination. It is suitable due to the fact that as the functional characteristics of the synthesized material the

Table 1
The results of determination of indium, gallium and zinc in $ZnGaIn_x$ by ICP-MS. ($1\text{-}a = 0.95$, n = 5). Introduced Ga/Zn for all samples 1 at.%.

Sample	Introduced In/Zn, at.%	Found Zn, ppb	Found In, ppb	Calculated In/Zn, at.% $s_r = 0.06$	Found Ga, ppb	Calculated Ga/Zn, at.% $s_r = 0.06$
1	0 In/Zn	520 ± 30	–	–	6.2 ± 0.4	1.1
2	1 In/Zn	480 ± 30	9.1 ± 0.5	1.10	5.3 ± 0.3	1.0
3	3 In/Zn	700 ± 35	42 ± 2	3.5	8.4 ± 0.5	1.1
4	5 In/Zn5	630 ± 40	56 ± 3	5.2	6.9 ± 0.4	1.0
5	10 In/Zn	680 ± 35	136 ± 7	11.2	7.4 ± 0.6	1.1

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