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Role of $ZnMn_2O_4$ phase in formation of varistor characteristics in ZnO:Mn ceramics

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Abstract. The samples ZnO:Mn were prepared using the conventional solid-state technique. To dope them with manganese, we used water solutions of $MnSO_4$ and $MnCl_2$. The properties inherent to both types of the obtained ceramics have been compared. It was found that the former demonstrated nonlinear current-voltage characteristics, whereas those of the latter were, in fact, linear. The analysis of EPR, diffuse reflectance and Raman spectra obtained for prepared ceramics allowed concluding that, in the samples doped with $MnSO_4$, formation of Mn-related phase, namely, $ZnMn_2O_4$ spinel occurred at ZnO grain boundaries under sintering. It has been ascertained that a thin layer of this substance separates adjacent ZnO grains, which provides appearance of the back-to-back Schottky barriers at grain boundaries and “varistor behavior” of current-voltage characteristics.

Keywords: ZnO:Mn ceramics, EPR, diffuse reflectance, Raman spectra.

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1. Introduction

Zinc oxide is known to be a wide-band-gap semiconductor (3.3 eV at 300 K) with a large exciton binding energy of 60 meV, high thermal and chemical stability, the absence of toxicity, high radiation hardness, and low cost. Due to these unique qualities as well as the possibility to modulate its characteristics by doping with different impurities, ZnO attracts much attention as a promising material for numerous technological applications. In recent decades, zinc oxide doped with manganese is extensively investigated because of the essential influence of this dopant on electrical, optical and magnetic ZnO properties. In particular, Mn is known to be one of “varistor formers” which enhances the nonlinearity of current-voltage (CV) characteristics and decreases the leakage current in ZnO-based varistors doped with other impurities [1]. It has been found that polycrystalline zinc oxide doped solely with Mn also demonstrates nonlinear CV characteristics and high resistivity [2–4]. At the same time, manganese is a deep donor in ZnO matrix which energy level resides at 2.0 eV below the conduction band edge [5] and, therefore, one might expect that doping with manganese should not influence on ZnO conductivity. In fact, ZnO single crystals doped with Mn under growth exhibit the same conductivity that the undoped ones [6]. Since one can think that high resistivity and varistor behavior in Mn-doped polycrystalline ZnO appear due to some processes that occur at grain boundaries under sample preparation. It has been found, indeed, that the nonlinearity of CV characteristics in ZnO-based varistors is caused by formation of back-to-back Schottky barriers at grain boundaries [1–4] and the adsorption of ambient oxygen has been proved to play the key role in this process [1, 7, 8].

It is known that ZnO surface adsorbs oxygen from ambient air. The capture of ZnO electrons by adsorbed oxygen atoms results in the appearance of a negative surface charge and formation of a depleted near-surface layer with reduced conductivity. One might expect that the same process would occur in any polycrystalline ZnO structure as a result of oxygen diffusion along grain boundaries, which would cause formation of intergranular barriers. However, both theoretical consideration [9] and experimental studies [6, 8, 10] have shown that intergranular barriers are absent in undoped polycrystalline ZnO and the doping by certain additives is necessary to obtain its varistor behavior. To account for this effect it has been supposed that under varistor preparation some impurity-related phase is formed in intergranular space, which separates adjacent ZnO grains and promotes oxygen diffusion along grain boundaries [1, 6, 8]. In fact, accumulation of Bi and the presence of Bi_2O_3 thin layer was found in ZnO:Bi ceramics with Bi content $N_{Bi} \geq 0.3$ at.% [1, 7]. In polycrystalline zinc oxide doped with manganese, the segregation of some Mn-related phases under sintering inside the 700…1200 °C temperature range was also shown [11–15] and tetragonal spinel $ZnMn_2O_4$ was found to be the dominant phase when sintering temperature was higher than 900 °C [13]. This phase reveals itself distinctly in XRD and Raman spectra at $N_{Mn} > 3$ at.% and is, in fact, imperceptible at $N_{Mn} < 1$ at.% [11, 12, 14, 15]. Nevertheless, a considerable increase of resistivity and appearance of nonlinear CV characteristic in polycrystalline ZnO:Mn are already observed at $N_{Mn} = 0.1$ at.% [2, 3, 8, 11, 14, 15]. One can suppose, therefore, that a thin Mn-related phase layer is still formed at grain boundaries, although it is not detected if using the conventional equipment. This assumption is confirmed by the fact that, after sintering the ceramics, a considerable part of the present in the charge manganese remains in the intergranular spaces [15]. The data obtained in the present work testify that it is intergranual $ZnMn_2O_4$ phase that is responsible for the varistor behavior of ZnO:Mn ceramics.

2. Experimental procedure

The samples were prepared from the mixture of ZnO powder (99.9 % purity) with $MnSO_4$ (A-type samples) or $MnCl_2$ (B-type samples) aqueous solution, Mn content in the charge being 0.3 and 3 at.%. The mixtures were dried at room temperature and compacted at $p = 1000$ kg/cm^2 to obtain rectangular plates that were then sintered in air for 3 hours at 1100 °C. After sintering, A-type ceramics acquired orange-brown color, and B-type ones became yellow.

In the sintered ceramics EPR, Raman and diffuse reflectance spectra as well as CV characteristics were measured at room temperature. EPR spectra were obtained using the upgraded X-band Varian E-12 spectrometer (~9.5 GHz) with the sensitivity limit of about 10^{12} EPR centers. The spectra were normalized on the sample mass and standard MgO:Mn reference signal intensity.

Raman spectra were excited with 457 nm solid-state laser and acquired using a single-stage spectrometer MDR-23 (LOMO) equipped with a cooled CCD detector (Andor iDus 420, UK). The laser power density on the samples was lower than 10 mW/cm^2 to prevent their thermal modification. A spectral resolution of ~3 cm^{-1} was determined from the Si phonon peak width of a single crystal Si substrate. The Si phonon peak position of 521.0 cm^{-1} was used as a reference for determining the position of Raman peaks.

Diffuse reflectance spectra were recorded with respect to the $BaSO_4$ standard by means of double-beam spectrometer UV-3600 UV-vis-NIR (Shimadzu Company) equipped with the integrating sphere ISR-3100. Obtained spectra were transformed into absorption ones using a standard program based on Kubelka–Munk ratio. For electrical measurements, ohmic indium electrodes were melted on freshly cleaved surfaces of the sample. The current was measured by home-made setup with sensitivity down to 10^{-11} A.

3. Results and discussion

EPR spectra of A-type and B-type samples with $N_{Mn} = 0.3$ at.% are shown in Fig. 1. Both spectra display the series of hyperfine lines grouped into characteristic five quasi-equidistant sextets, which testifies to formation of isolated paramagnetic Mn_{Zn}^{2+} centers in ZnO host lattice [16], the intensity of Mn_{Zn}^{2+}-related lines being slightly higher in B-type samples with respect to that in A-type ones.

At the same time, CV characteristics of obtained ceramics are different: the A-type sample demonstrates varistor behavior, whereas CV characteristic of B-type sample, is, in fact, linear (Fig. 2).

The difference is also observed in diffuse reflectance spectra for A-type and B-type samples (Fig. 3). One can see that in both samples, side by side with intrinsic UV absorption, a broad unstructured extrinsic band is present in the visible spectral region. This absorption is usually observed in zinc oxide doped with manganese and is ascribed to the transitions of electrons in *c*-band from Mn_{Zn}^{2+} ions due to their photoionization [17].

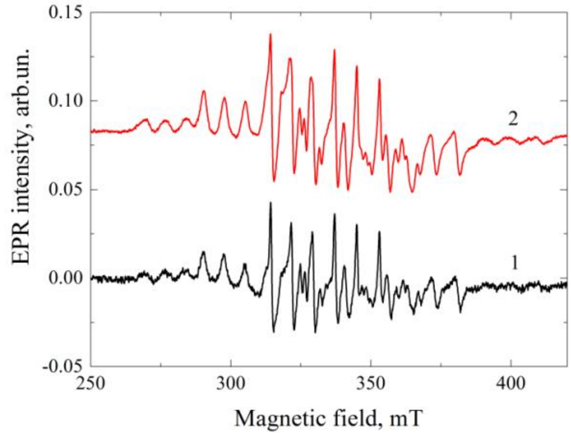

Fig. 1. EPR spectra for A-type (*1*) and B-type (*2*) ceramics with $N_{Mn} = 0.3$ at.%.

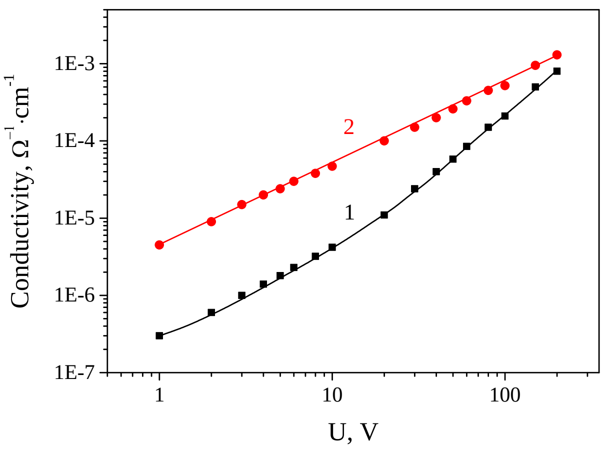

Fig. 2. CV characteristics of the A-type (*1*) and B-type (*2*) samples with $N_{Mn} = 0.3$ at.%.

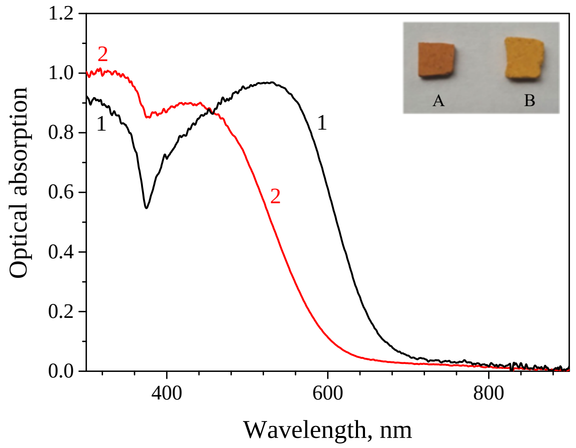

Fig. 3. Normalized optical absorption spectra of A-type (*1*) and B-type (*2*) ceramics with $N_{Mn} = 0.3$ at.%. Insert shows the ZnO:Mn samples of types A and B after sintering.

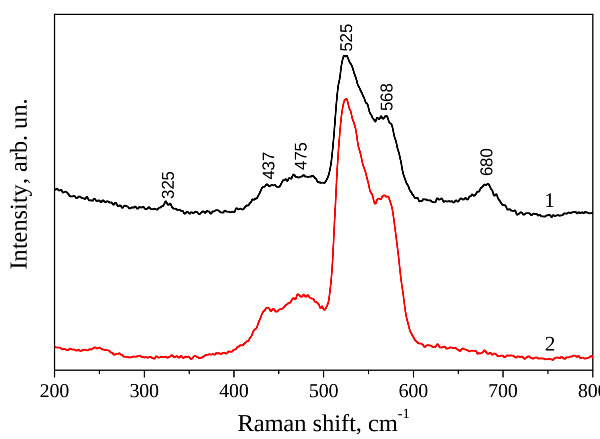

Fig. 4. Raman spectra of A-type (*1*) and B-type (*2*) samples with $N_{Mn} = 3$ at.%. ($\lambda_{exc} = 457$ nm).

As Fig. 3 shows, in the A-type sample, the extrinsic absorption band is broader and red-shifted with respect to that in the B-type one, which is in accordance with the color of the samples. This difference can be explained by different chemical reactions taking place under sintering. In the A-type samples, appearance of MnO_2 due to the thermal decomposition of $MnSO_4$ (*via* reaction $MnSO_4 = MnO_2 + SO_2$) and further reaction of MnO_2 with ZnO takes place, which results in formation of $ZnMn_2O_4$ phase [18]. At the same time, in the B-type samples, the reaction $MnCl_2 + Zn = Mn + ZnCl_2$ with further $ZnCl_2$ sublimation and Mn diffusion in ZnO grains occurs. It should be thought, therefore, that the red-shift of the extrinsic absorption band in the A-type sample is caused by superposition of Mn_{Zn}^{2+}-related absorption and that caused by $ZnMn_2O_4$ phase. In fact, the optical absorption spectrum of $ZnMn_2O_4$ spinel cited in the literature [18] is similar to that shown in Fig. 2. It should be noted that $ZnCl_2$ sublimation would result in the increase of ZnO grains resistivity because of Zn extraction and the decrease of interstitial Zn concentration. In fact, the resistivity of B-type samples is noticeably higher than that of undoped ZnO ceramics [8, 15].

To verify that $ZnMn_2O_4$ phase is formed indeed in the samples doped using $MnSO_4$, Raman spectra for A-type and B-type ceramics with $N_{Mn} = 3$ at.% were measured (Fig. 4). One can see that noticeable peaks at 325 and 680 cm^{-1} that are characteristic for $ZnMn_2O_4$ spinel [11, 13, 15, 18] are present in A-type sample spectra and are absent in that for B-type sample.

Thus, the analysis of the characteristics of ZnO:Mn samples doped with Mn from different sources and the comparison of obtained results with literature data give the possibility to conclude that formation of $ZnMn_2O_4$ layer in the integranular space between ZnO grains under sintering is responsible for varistor effect in ZnO:Mn ceramics.

4. Conclusions

ZnO:Mn samples were formed of the mixture of ZnO powder with $MnSO_4$ (A-type samples) or $MnCl_2$ (B-type samples) aqueous solution and sintered in air for 3 hours at 1100 °C, manganese content in the charge N_{Mn} being 0.3 and 3 at.%. It was found that the A-type ceramics had orange-brown color, whereas the B-type ones with the same N_{Mn} were yellow. To understand the origin of these differences, EPR, diffusion reflectance, and Raman spectra as well as current-voltage characteristics for both types of ceramics were measured and compared. Our analysis of the obtained results in common with available literature data led to the conclusion that, under ceramics sintering, in A-type samples Mn-related phase, namely, spinel $ZnMn_2O_4$ was formed at ZnO grain boundaries, whereas the similar process took no place in B-type samples. It is stated that a thin layer of this secondary phase separates adjacent ZnO grains, which promotes oxygen adsorption and formation of Schottky barriers at grain boundaries.

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Роль фази $ZnMn_2O_4$ в утворенні варисторних характеристик у кераміці ZnO:Mn

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Анотація. Традиційним твердофазним методом виготовлено кераміку ZnO:Mn. Для легування манганом використано водний розчин $MnSO_4$ або $MnCl_2$. Проведено порівняння властивостей кераміки обох типів. Виявлено, що зразки першого типу демонструють нелінійні вольт-амперні характеристики, тоді як зразки другого типу мають, фактично, лінійні. Аналіз спектрів ЕПР, дифузного відбивання та комбінаційного розсіювання світла дозволив зробити висновок, що у зразках, легованих з використанням $MnSO_4$, під час спікання на границях зерен ZnO відбувається утворення фази, пов'язаної з Mn, а саме – шпінелі $ZnMn_2O_4$. Установлено, що тонкий шар цієї сполуки розділяє сусідні зерна ZnO, що приводить до появи подвійних бар'єрів Шотткі на границях зерен і «варисторної поведінки» вольт-амперних характеристик.

Ключові слова: кераміка ZnO:Mn, спектри ЕПР, дифузне відбивання, комбінаційне розсіяння світла.