Ferromagnetism of Nanostructured Zinc Oxide Films

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Abstract—The paper presents a review of the causes of the occurrence of ferromagnetic properties in zinc oxide. It is shown that ferromagnetism only occurs in polycrystals at a fairly high density of grain boundaries. The critical grain size is about 20 nm for pure ZnO and over 1000 nm for zinc oxide doped with manganese. The solubility of manganese and cobalt in zinc oxide increases considerably with diminishing grain size. Even at the critical grain size, the ferromagnetic properties depend significantly on the film texture and the structure of intercrystalline amorphous layers.

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INTRODUCTION

Grain boundaries (GBs) in polycrystalline materials affect their basic physical and technological properties, such as strength, ductility, corrosion resistance, and diffusion permeability. One of the factors which controls the influence of GBs on the properties of polycrystals is their high adsorption capacity. As early as in the 1950s, McLean predicted that the adsorption of the second component on GBs should increase its total solubility and, therefore, cause the shift of lines on phase diagrams [1]. However, for the materials whose grain size exceeds a few microns, this effect is vanishingly weak. The recent advent of nanocrystalline materials, especially those in which multilaver adsorption can occur on GBs, resulting in the formation of interlayers of grain-boundary phases (for example, in bismuth-doped zinc oxide used to produce varistors [2]), introduces possible variations into the phase diagrams due to the high adsorption capacity of GBs.

Nanocrystalline oxides are very interesting objects, which can be used as semiconductor membranes, materials for gas sensors, and solid electrolytes of fuel elements, as well as protective, decorative, and functional coatings (for example, energy-saving or selfcleaning windows); they are also applied in solid-state electronics. The theoretical prediction of ferromagnetic properties of zinc oxide doped with cobalt, manganese, or iron at room temperature by Tomasz Dietl [3] gave rise to an avalanche of experimental works [4]. This is explained by the fact that the manifestation of high-temperature ferromagnetism in a transparent wide-band semiconductor such as zinc oxide makes it an extremely promising material for spintronics, since it is fundamentally possible to control the electrical properties of the material by applying the magnetic field, as well as its magnetic properties by applying the electric field. However, as is noted in review [4], the presence or absence of high-temperature ferromagnetism in zinc oxide is related to crystalline defects and, to a large extent, such interelation remains inapprehensible. Therefore, the influence of the effect of GBs on ferromagnetism in zinc oxide is one of the most topical trends in the modern condensed-matter physics and materials science.

EXPERIMENTAL

Thin zinc oxide films doped with cobalt or manganese were deposited on aluminum-foil substrates by the fluid ceramics method. A mixture of fluid organic acids and metal ions was applied to a substrate, then dried at 150° C. Zinc (II) butanoate dissolved in the organic solvent (the zinc concentration was 1 to 4 kg/m³) was used as a precursor to the formation of pure zinc oxide films. To synthesize zinc oxide films doped with 0.1 and 10 at % of Mn, the zinc (II) butanoate solution was mixed with manganese (III) butanoate solution in the corresponding proportions. The butanoate precursor was applied to polycrystalline aluminum foils and sapphire monocrystals with a (102) orientation. Then, the films were subjected to pyrolysis in air or argon at 500, 550, and 600°C. The oxidation of organic acid films occurred simultaneously with their pyrolysis. As a result, thin films of zinc oxide doped with cobalt or manganese were formed; they were pore-free and contained equiaxed zinc oxide grains (Fig. 1). The films were slightly green and transparent. The film thickness was determined by electron-probe X-ray microanalysis (EPMA) and transmission electron microscopy (TEM) and varied whithin 50-200 nm. The cobalt concentration in the films was 0-52 at % and that of manganese was 0-47 at %. The concentration of cobalt, manganese, and zinc in the oxide films was measured by atomic absorption spectroscopy using a PerkinElmer spectrometer and EPMA using a Tescan Vega TS5130 MM electron microscope equipped with an Oxford Instruments energy-dispersion spectrometer. TEM examination was carried out using a JEM-4000FX microscope at an accelerating voltage of 400 kV. TEM was applied to study the film crystalline structure, especially on interfaces, and to detect possible pure cobalt or manganese oxide particles, as well as to measure the grain size in the pure and doped zinc oxide films. X-ray diffraction was studied in Fe $K\alpha$ radiation using a Siemens diffractometer with a graphite monochromator and a flow gas detector. The grain size was calculated from the angular dependence of the line broadening [5]. The grain size in the specimens under study was 10 ± 2 nm. The magnetic properties were measured by a SQUID (Quantum Design MPMS-7 and MPMS-XL) superconductive quantum interferometer. The magnetic field was applied parallel to the specimen plane. The diamagnetic signal induced by the specimen holder and substrate was subtracted carefully from the magnetization curves.

RESULTS AND DISCUSSION

Increase of Total Solubility of Second Component in a Polycrystal Due to Grain Refinement

With increasing the content of the doping component x, the solubility limit of two-component and multicomponent alloys is achieved at a certain concentration c_s . At higher concentrations c_s , the second phase appears in the grain bulk. As c continues to increase, only the amount of the second phase increases, while that of the first phase remains equal to c_s . The solubility limit in the bulk increases with increasing temperature. The simplest way to measure c_s is to observe variations in the lattice parameter of the solid solution by, e.g., X-ray diffractometry. The lattice parameter changes continuously, i.e., it can increase or diminish, as x grows to c_s . At $x > c_s$ the lattice period does not change and the intensity maxima corresponding to the second phase appear in the diffraction pattern.

If an alloy contains the surfaces or interfaces enriched in the second component, the total concentration of this component x_t exceeds its concentration x_v in the grain bulk of the solid solution. The difference between x_t and x_v grows with increasing specific area of



Fig. 1. Dark-field electron microscopy image of thin nanocrystalline zinc oxide film obtained by fluid ceramics method.

external surfaces and interfaces, e.g., when grain refinement occurs. If the grain size is fairly small, the difference between x_t and x_v can be measurable. This is explained by the fact that X-ray diffractometry (XRD) only registers diffraction from bulk phases. The component located in thin surface layers or in the interfaces remains invisible for the XRD. The intensity peaks appear on the diffraction pattern only when the coherently scattering domain is sufficiently large (the grain size is about 5 nm or greater). At the same time, XRD is capable of measuring the grain size using the angular dependence of the peak width.

McLean assumed that, in fine-grained materials, the total solubility limit c_{sa} is higher than the bulk solubility limit c_s [1]. He calculated this difference for the Fe–C system with a grain size of $1-10 \,\mu\text{m}$ for the case of simple Langmuir-type grain-boundary segregation [1]. There is a great deal of evidence that, in microand nanograined materials, $c_{sa} > c_s$ [6–11]. However, XRD studies of the shift of the solubility $c_{sa}-c_s$ depending on the grain size d are highly labor-intensive and, to our knowledge, have never been carried out. ZnO presents an excellent possibility for these investigations and is widely used as a transparent conductive oxide in thin-film semiconductor technologies and as a material for varistors (ZnO doped with Bi₂O₃) and gas sensors. Moreover, when being applied as ferromagnetic semiconductor, it is a promising material for future spintronics. Ferromagnetic semiconductors enable electric control over magnetic states and the magnetic transformation of electric signals. In 2000, T. Dietl et al. theoretically predicted that ZnO doped with small amounts of magnetic impurities, such as manganese or cobalt, possesses ferromagnetic properties [3]. This work gave rise to numerous experimental studies and over 1200 papers have been published since then that deal with low-doped semiconductors. The presence or absence of ferromagnetism in doped ZnO depends on the method of synthesis. These studies make it possible to calculate the dependence of $c_{sa}-c_s$



Fig. 2. Dependence of lattice parameter c of zinc oxide films doped with cobalt on its concentration [12].



Fig. 3. Variations in zinc oxide lattice period with increasing manganese concentration for different grain sizes [13].

on the grain (particle) size d, since the presence or absence of the second phase (manganese or cobalt oxide) was checked experimentally in specimens in almost all works dealing with the ferromagnetism of zinc oxide.

The solubility limit of these elements in nanocrystalline ZnO films with a grain size of 20 nm was determined from the variations in the lattice period of zinc oxide with increasing cobalt or manganese concentration. The lattice period of zinc oxide grows linearly to 33 at % of Co (Fig. 2) [12]. Above 33 at % of Co the second phase, Co₂O₃ with the cubic lattice appears and the period of the wurtzite zinc oxide lattice ceases to increase as the cobalt concentration rises. This means that the solubility limit c_{sa} of cobalt in thin zinc oxide films is 33 at % of Co at 550°C (the synthesis temperature of the films). The solubility limit of manganese is approximately 33 at % of Mn (Fig. 3) [13]. The comparison of these values with the literature data (Fig. 3) shows that the finer the grain size, the slower the growth in the lattice period with increasing manganese concentration and the higher the concentration at which the solubility limit is reached, i.e., when the second phase Mn_3O_4 appears. We explain this phenomenon by the adsorption of the second component in the grain boundaries.

To discover ferromagnetism in doped ZnO, it is important to be sure that the oxide is free of any second phase particles capable of affecting the magnetic behavior of the specimen. This meant that each published work of the study of ferromagnetism in ZnO reports the data on the concentration of the doping element and notes the presence or absence of the second phase. These data have allowed us to plot the lines



Fig. 4. Solubility limit of cobalt in zinc oxide polycrystals with grain size of (a) over 1000 nm and (b) below 20 nm [12]. Solid symbols correspond to the single-phase specimens, open symbols correspond to the two-phase specimens, and asterisks correspond to the solubility limit.

of the solubility limit of cobalt and manganese in zinc oxide for various grain sizes (Fig. 4 and 5) [12, 13]. Figure 4 shows the lines of the solubility limit of cobalt for a grain size of more than 1000 nm and less than 20 nm, as well as the experimental points. Figure 5 shows the lines of the solubility limit of cobalt and manganese for various grain sizes without experimental points. It is clearly seen how rapidly the total solubility of the cobalt and manganese increases with diminishing grain size.

In the specimens without grain boundaries and only an extended external surface (nanopowders, nanowires, and tetrapods), the total solubility also increases with diminishing particle size, but much slower than in the case of polycrystals with grain boundaries (see Fig. 6). The estimations of the adsorption capacity of grain boundaries and the external surface show that an adsorption layer 2–4 Co or Mn monolayers in capacity is formed on the external surfaces and over ten monolayers appear at the grain boundaries [12, 13].

Thus, the accumulation of cobalt and manganese on GBs and free surfaces sharply shifts the solubility limit of these elements in zinc oxide towards higher concentrations. For example, at 550° C, the total solubility of cobalt does not exceed 2 at % of Co in zinc oxide bulk and amounts to 33 at % in the nanocrystalline specimen with a grain size of less than 20 nm. The solubility of manganese at 550° C increases from 12 to 40 at %. The shift of the solubility limit in the polycrys-



Fig. 5. Solubility limit of (a) cobalt [12] and (b) manganese [13] in zinc oxide polycrystals with different grain sizes.

tal with GBs is greater than in nonsintered powder free of GBs, while the grain size is the same. This means that GBs are capable of accumulating approximately two to four times greater amounts of cobalt or manganese than free surfaces. Therefore, the phase diagrams of the substances with a grain size of less than 1000 nm should be examined again. Especially sharp changes in the phase diagrams can be expected at a grain size of less than 100 nm.

Critical Grain Size for Occurrence of Ferromagnetic Properties in Zinc Oxide

Although over 1000 works that deal with the discovery of ferromagnetism in pure and doped zinc oxide have been published, the experimental results are very contradictory. An analysis of the literature data shows that pure and doped zinc oxide monocrystals and the specimens produced by the sintering common coarsegrain powders (with a particle size of over 10 μ m) always remain diamagnetic or paramagnetic. The

specimens produced by pulsed laser deposition (PLD) almost always demonstrate ferromagnetism at room temperature. The zinc oxide specimens synthesized by methods of wet chemistry or chemical vapor deposition (CVD) possess intermediate properties; they can be both paramagnetic and ferromagnetic.

We assumed that the presence of ferromagnetic properties in zinc oxide correlates with the specific area of grain boundaries in unit volume s_{GB} . We determined that this characteristic is based on the data reported in works on ferromagnetism in both pure and manganese-doped zinc oxide [14]. The results of these calculations for pure and manganese-doped zinc oxide are shown in Fig. 7 in the temperature–specific densities of boundaries s_{GB} coordinates. Here, "temperature" refers to the temperature of the annealing or fabrication of specimens.

The results clearly demonstrate the existence of the dependence of the ferromagnetic properties of pure and doped zinc oxide specimens on the specific area of boundaries. The specimens only possess ferromagnetic properties if the specific area of the boundaries exceeds the critical value s_{th} . Free surfaces do not result in ferromagnetism, even if their specific area is great and oxide particles are very small, but no grain boundaries are present in the specimen. If zinc oxide nanoparticles or nanowires are not completely sintered and free of grain boundaries, they also do not possess the ferromagnetic properties. Similar results were obtained for the specimens of zinc oxide doped with cobalt. Thus, the presence of manganese or cobalt is not necessary for the ferromagnetic properties to occur in zinc oxide. Even pure zinc oxide can be ferromagnetic; the fine grain size or high specific area s_{GB} play a crucial role, rather than doping with magnetic atoms, as was initially assumed [3]. Nevertheless, the presence of manganese or cobalt in the zinc oxide lattice facilitates transition to the ferromagnetic state and shifts the critical size towards greater grain sizes (Fig. 7). For example, in a number of works in which the specific grain size fell between the critical size for the pure zinc oxide and that doped with manganese, paramagnetic properties were observed in pure zinc oxide and ferromagnetic properties were observed in specimens doped with manganese [15, 16].

Figure 8 shows the magnetization curves for the pure zinc oxide films and films doped with 0.1 and 10 at % manganese (in units of $10^{-3} \mu_B/f.u.$ at room temperature). These curves were obtained after the subtracting the magnetic contribution of the substrate and specimen holder. The magnetization is $2 \times 10^{-3} \mu_B/f.u. = 0.16$ emu/g for the zinc oxide films doped with 0.1 at % manganese, $0.8 \times 10^{-3} \mu_B/f.u. = 0.04$ emu/g for the zinc oxide films doped with 10 at % manganese, and $1 \times 10^{-3} \mu_B/f.u. = 0.06$ emu/g for pure zinc oxide deposited on an aluminum substrate. Thus, the extremely small grain size and, hence, high specific



Fig. 6. Solubility limit of (a) cobalt [12] and (b) manganese [13] in zinc oxide powders with different particle sizes.

density of grains in the studied pore-free films make it possible to observe the ferromagnetic behavior of both pure and doped zinc oxide. The first signs of the ferromagnetic behavior of pure zinc oxide films were obtained quite recently; our work was the second study in which ferromagnetism was observed in undoped zinc oxide.

The saturation magnetization grows linearly with increasing thickness, i.e., the mass of a zinc oxide film. The magnetization curves of pure zinc oxide show hysteresis with a coercive force H_c of about 0.02 T for the zinc oxide film on the sapphire substrate (Fig. 9a) and about 0.01 T for the zinc oxide film on the aluminum substrate (Fig. 9b). Figure 9 presents only the magnified middle part of the magnetization curves to

illustrate clearly the value of the coercive force. These values are close to the coercive force found in works of other authors in pure zinc oxide ($H_c = 0.005-0.02$) or exceed it. At 40 K, the saturation magnetization of the pure zinc oxide films deposited on a sapphire substrate is only by 40% higher than that at the room temperature. This means that the Curie temperature of the films under study greatly exceeds room temperature.

Effect of Doping and Grain Boundary Structure on Ferromagnetic Behavior of Zinc Oxide Films

Among doped magnetic semiconductors, zinc oxide doped with manganese is one of the most promising materials for applications in spintronics, since



Fig. 7. Ferromagnetic (solid symbols) and paramagnetic or diamagnetic (open symbols) behavior of films of (a) pure zinc oxide and (b) zinc oxide doped with manganese depending on specific area of grain boundaries s_{GB} (ratio of area of boundaries to volume) at various temperature of specimen synthesis *T*. Vertical dashed lines mark threshold value s_{th} . Large symbols are experimental data from our work [14].

manganese ions possess the maximum magnetic moment among 3d transition metals. Moreover, manganese has an almost completed 3d band, which makes it possible to achieve the stable spin-polarized state. The saturation magnetization depends nonmonotonically on the manganese concentration (Fig. 10) [17]; it increases by almost three orders of magnitude when a very small amount of manganese is added



Fig. 8. Magnetization of films of pure zinc oxide and zinc oxide doped with 0.1 and 10 at % of manganese at room temperature (in [14]).

(0.1 at %) to pure zinc oxide. As the manganese concentration continues to increase, the saturation magnetization drops rapidly and becomes nearly indistinguishable from the background concentration at 5 at % of manganese. At a greater amount than 5 at % of manganese, the magnetization increases again. The saturation magnetization drops again to the background values only in the vicinity of 30 at % of manganese, when the second phase Mn_3O_4 appears in zinc oxide with the wurtzite lattice in addition to manganese solid solution. We assume that, at small manganese concentrations, the growth in the saturation magnetization results from the injection of bivalent manganese ions and charge carriers into pure zinc oxide. The decrease of the saturation magnetization in the range of 0.1-5 at % of manganese is caused by an increase in the share of tri- and quadricvalent manganese ions. The repeated growth of the saturation magnetization at greater concentrations than 5 at % of manganese is due to to the formation and growth of multilayer segregation films rich in manganese at the grain boundaries of zinc oxide.

Similar nonmonotonic variations in the magnetization with increasing manganese concentration are reported in the literature and are observed in nanocrystalline specimens of manganese obtained by other methods. However, the minima and maxima of the magnetization are found at other manganese concentrations. This can be explained by different topologies of the grain-boundary network in these materials.

Figure 11 shows the bright-field micrographs of the doped zinc oxide films with 10 at % of Mn (Fig. 11a) and 15 at % of Mn (Fig. 11b) obtained by high-resolution transmission electron microscopy [18]. The direct resolution of the lattice makes crystalline zinc oxide grains with the wurtzite lattice visible. It can be clearly seen in Fig. 11a that the amorphous phase interlayers are located in the boundaries between these grains. With

Fig. 9. (a) Magnetic hysteresis at room temperature for pure zinc oxide films deposited on sapphire single crystal. (b) Magnetic hysteresis at room temperature for pure zinc oxide film deposited on aluminum foil. Only the magnified middle part of the magnetization curves is presented to demonstrate clearly coercive force values.

Fig. 10. Dependence of saturation magnetization of zinc oxide doped films on manganese concentration [17].

Fig. 11. Bright-field micrographs of films of zinc oxide doped with manganese obtained by high-resolution transmission electron microscopy. (a) Zinc oxide with 10 at % of manganese. Amorphous interlayers between nanocrystalline ZnO grains are seen. (b) Zinc oxide with 15 at % of manganese. Crystalline ZnO grains are surrounded by amorphous interlayers. Inserts show Fourier transform patterns for amorphous and crystalline areas [18].

increasing manganese concentration from 10 to 15 at %, the amount of the amorphous phase grows. It can clearly be seen from the comparison of the structures presented in Figs. 11a and 11b. Thus, one of the grains of zinc oxide with the wurtzite lattice in Fig. 11a

(in the middle of the photo) is surrounded on all sides by an amorphous area rich in manganese. Since the amorphous interlayers in the specimen with 15 at % of Mn are already thick, we have managed to obtain Fourier transform patterns for the amorphous and crystalline areas. The corresponding crystalline grains (to the left and right) and the amorphous interlayer (in the middle) are designated as A, B, and C in Fig. 11b.

Figure 11 demonstrates clearly what happens when manganese is gradually added to nanocrystalline zinc oxide. Some of the manganese atoms fall into the grain lattice during doping and contribute to the shift of X-ray diffraction peaks from the coherent-scattering regions (the grains with the wurtzite lattice). The remaining manganese atoms (approximately twothirds) fall into the amorphous interlayers that surround and separate the grains. These amorphous interlayers become thicker with increasing manganese concentration. Our quantitative estimation shows that, at 30 at % of Mn, when the solubility limit for a grain size of 20 nm is reached, the thickness of the grain-boundary interlayers is six to ten monolayers of manganese oxide, while that of the layers on the external surface is two monolayers [13]. This situation differs radically from the case of one-layer McLean adsorption (on the surface of GBs).

The morphology of the amorphous areas between zinc oxide grains enriched in manganese differs considerably from that of very homogeneous and uniformly thin amorphous interlayers of the grain-boundary prewetting phases in the ZnO:Bi₂O₃ specimens obtained by fluid-phase sintering [19]. Thus, the amorphous areas in the specimen with 15 at % of Mn (Fig. 11b) surround some zinc oxide grains on all sides and only partially penetrate between the remaining grains. This microstructure strongly resembles the morphology of two-phase polycrystals, in which the second phase fully wets some boundaries and partially wets the remaining boundaries.

It is well known from the experiments with metal alloys that the distribution over misorientation and orientation of grain boundaries significantly changes the behavior of polycrystals. We compared the magnetic properties of nanocrystalline zinc oxide films with the same grain size, which was considerably smaller than the threshold value, but with different misorientation and orientation distributions of boundaries.

Figure 12 shows the X-ray diffraction spectra for the thin zinc oxide films deposited on the sapphire monocrystals with orientation (102) and annealed in air (the upper curve) or argon (the lower curve) [20]. The X-ray spectrum for the film annealed in argon (the lower curve) contains three peaks, which correspond to the reflections 100, 002, and 101 of the hexagonal wurtzite lattice of zinc oxide. The X-ray diffraction spectrum from the film annealed in air (the upper curve in Fig. 12) contains practically only one peak that corre-

Fig. 12. X-ray diffraction curves for ferromagnetic (upper curve) and diamagnetic (lower curve) zinc oxide thin films deposited on sapphire substrate with orientation (102) and annealed in air (upper curve) and argon (lower curve) [20].

sponds to the 002 reflection from zinc oxide with a hexagonal wurtzite structure. This means that the film synthesized in air has a pronounced texture.

Figure 13 shows the magnetization curves for thin zinc oxide films annealed in air (black triangles) and argon (black circles) [20]. The black triangles correspond to the magnetization curve obtained after the subtraction of the contribution of the uncovered sapphire substrate. The film annealed in air possesses pronounced ferromagnetic properties and has a saturation magnetization of about 12×10^{-6} emu (at applied fields of over 6 T). The film annealed in argon does not demonstrate the ferromagnetic behavior and remains diamagnetic. The light circles show the magnetization of the zinc oxide film annealed in air after the subtraction of the diamagnetic contribution of the substrate. This ferromagnetism of the substrate is governed by the residual ferromagnetic impurities. A comparison of these two curves (the black and white circles) shows that the zinc oxide film annealed in argon has almost no additional ferromagnetism compared to the substrate.

A comparison of the data in Figs. 12 and 13 shows that the zinc oxide film with a pronounced texture possesses ferromagnetic properties and the nontextured (or weakly textured) film remains diamagnetic. These results demonstrate that the specific area of grain boundaries in the unit volume of nanocrystalline zinc oxide films is not the only factor that governs the ferromagnetic behavior of the material. This means that even if the grain size is much smaller than the critical value necessary for ferromagnetic behavior also depends on the presence or absence of the film texture. This means that the ferromagnetism of zinc oxide is governed by not only the presence of grain boundaries, but also their structure.

Fig. 13. Magnetization curves for zinc oxide thin films annealed in air (F, ferromagnetic films,) and Ar (D, diamagnetic films,). Black triangles correspond to magnetization curve obtained after subtraction of contribution of bare sapphire substrate [20].

We also studied the nondoped zinc oxide films obtained by the thermal pyrolysis of butanoate precursors in argon at 650°C for 0.5 h (1) and at 550°C for 24 h (2) [21]. The film thickness was 690 nm (1) and 370 nm (2), respectively. Figure 14 shows the magnetization curves M(H) for thin zinc oxide films (1) and (2). The magnetization on these curves was measured together with the sapphire substrate. The values of the magnetization in Fig. 14a are reduced to the same area of the films and given in emu/cm². Figure 14b illustrates the middle portions (at low values of the applied magnetic fields) of the magnetization curves of films (1) and (2) without the contribution of the substrate; they are given in emu/cm³. Thus, specimen (2) possesses more pronounced ferromagnetic properties.

Figure 15 shows the bright-field high-resolution electron microscopy image of zinc oxide film (1) annealed in argon at 650°C for 0.5 h [22]. This specimen demonstrates very weak ferromagnetism with $M_{\rm s}(1) = 27 \times 10^{-6} \, {\rm emu/cm^2}$ (Fig. 14a). The crystalline zinc oxide grains separated by a thin (2-5 nm)amorphous film are clearly visible in the micrograph. The electron diffraction pattern for this specimen contains the reflection for the wurtzite phase of zinc oxide and the weak halo of the amorphous phase (Fig. 15b). Figure 16a illustrates the bright-field highresolution electron microscopy image of zinc oxide film (2) annealed in air at 550°C for 24 h. The film possesses ferromagnetic properties and has a saturation magnetization M_s (2) = 75 × 10⁻⁶ emu/cm² (Fig. 14a). It can be clearly seen that the crystalline grains of zinc oxide with wurtzite structures are surrounded by wide amorphous interlayers. The electron

Fig. 14. (a) Magnetization curves M(H) for zinc oxide thin films (1), and (2), at room temperature. Magnetization is measured together with sapphire substrate and is given in emu/cm². (b) Middle portions (at low applied fields) of magnetization curves for films (1) and (2) without substrate contribution in emu/cm³ [21].

diffraction pattern (Fig. 5.10b) contains reflections from the wurtzite lattice and an intensive halo of the amorphous phase.

Thus, the saturation magnetization of the ferromagnetic zinc oxide specimens increases distinctly with the increasing amount of the amorphous phase between the crystalline grains of zinc oxide. The dependences of the saturation magnetization on the manganese concentration differ for nanocrystalline zinc oxide specimens doped with manganese and produced by different methods [17]. In all likelihood, nonuniformly distributed lattice defects are not the only cause of ferromagnetism in zinc oxide. Moreover, the proper proportion and topology of the interpenetrating crystalline and amorphous phases are necessary for ferromagnetic properties to occur in pure zinc oxide.

In conclusion, we note that, in zinc oxide, grain boundaries not only induce a shift of the solubility limit

Fig. 15. (a) Bright-field high-resolution electron microscopy image of zinc oxide film (1) annealed in argon at 650° C for 0.5 h. Crystalline zinc oxide grains separated by thin 2–5 nm amorphous film are seen. (b) Electron diffraction pattern with reflections for wurtzite phase of zinc oxide and weak halo of amorphous phase [21].

lines with diminishing grain size, but also cause its ferromagnetic behavior. Both the high specific area of grain boundaries (their quantity) and the structure of the boundaries, as well as their orientation and misorientation distribution (their quality), are important.

Fig. 16. (a) Bright-field high-resolution electron microscopy image of zinc oxide film (2) annealed in argon at 550°C for 24 h. Crystalline zinc oxide grains with wurtzite structure are surrounded by wide amorphous interlayers. (b) Corresponding electron diffraction pattern with reflections from wurtzite lattice and intensive halo of amorphous phase [22].

CONCLUSIONS

The accumulation of cobalt and manganese on GBs and free surfaces drastically shifts their solubility limit in zinc oxide towards higher concentrations. For example, at 550°C, the total solubility of cobalt does not exceed 2 at % of Co in the bulk of zinc oxide and

it is 33 at % in the nanocrystalline specimen with a grain size of less than 20 nm. The solubility of manganese at 550°C increases from 12 to 40 at %. The shift of the solubility limit in the polycrystal with GBs is greater than in the nonsintered powder free of GBs, the grain size being the same. This means that GBs can accumulate approximately two to four times more cobalt or manganese than free surfaces. Thus, phase diagrams of the substances with a grain size of less 1000 nm should be studied again. Especially sharp changes in the phase diagrams may occur at a grain size of less than 100 nm.

Numerous experimental data on the ferromagnetic behavior of zinc oxide have been analyzed from the viewpoint of the presence of grain boundaries in spec imens. The ratio of the area of the boundaries to the crystal volume s_{GB} has been determined. In zinc oxide, ferromagnetism only occurs if the area of the grain boundaries in the unit volume of the material exceeds the critical value s_{th} . The critical value s_{th} for ZnO doped with manganese is almost two orders of magnitude greater than for pure zinc oxide. The ferromagnetic properties of pure and manganese-doped zinc oxide with a grain size of 20 nm have been determined experimentally.

The dependence of the saturation magnetization on the manganese concentration is very nonmonotonic. At low manganese concentrations, the saturation magnetization growth is caused by the injection of bivalent manganese ions and charge carriers into pure zinc oxide. The decrease of the saturation magnetization between 0.1 and 5 at % of manganese results from an increase in the fraction of trivalent and quadrivalent manganese ions. The repeated increase in the saturation magnetization at a manganese concentration of over 5 at % is due to to the formation and growth of multilayer segregation films rich in manganese on grain boundaries of zinc oxide. The pattern of the dependence of the saturation magnetization on the manganese concentration differs for nanocrystalline manganese-doped zinc oxides produced by various methods and is governed by the topology of the grainboundary network (ferromagnetic grain-boundary foam) in a zinc oxide polycrystal.

The structure of the grain boundaries in doped zinc oxide, which form the "grain-boundary foam" and are responsible for the occurrence of the ferromagnetic behavior of zinc oxide, has been studied experimentally. The amorphous interlayers are found on the grain boundaries; they do not contribute to the shift of X-ray diffraction peaks from coherent-scattering regions (grains with the wurtzite lattice). As a result, only onethird of the doping manganese atoms are incorporated into the wurtzite lattice of crystallites at a grain size of 20 nm and about two-thirds of them fall into the amorphous interlayers surrounding the grains. The specific area of grain boundaries is not the sole factor that governs the ferromagnetic behavior of zinc oxide. The saturation magnetization depends on the film texture and, hence, the distribution over misorientation and orientation of grain boundaries.

The presence of a grain-boundary network with a specific area in zinc oxide is a necessary but not sufficient condition for the occurrence of the ferromagnetic properties in pure oxide. The microstructure of intergranular layers can be varied by changing the conditions of synthesis. The saturation magnetization M_s depends on the structure of the intergranular layers in zinc oxide and grows with an increasing amount of the intergranular amorphous phase. In all likelihood, the proper combination of the interpenetrating crystalline and amorphous phases is a condition for the occurrence of ferromagnetic properties in zinc oxide.

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