Influence of texture on the ferromagnetic properties of nanograined ZnO films

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The pure ZnO thin films were deposited by the wet chemistry (‘liquid ceramics’) method from the butanoate precursors on the single-crystalline (102) sapphire substrates. The films annealed in air (550 °C, 24 h) after butanoate pyrolysis have pronounced texture, and they reveal the ferromagnetic behaviour. Argon annealed films (650 °C, 30 min) exhibit randomly oriented grains, where the ferromagnetism of these non-textured films is almost equal to that of bare substrate. In both cases the films consist of dense equiaxial nanograins with size ~20 nm. We observed that grain boundaries (GBs) and related vacancies are the intrinsic origin for RT ferromagnetism in polycrystals [Straumal et al., Phys. Rev. B 79, 205206 (2009)]. Present results demonstrate that not only the specific area of GBs in nanograined ZnO alone determines the ferromagnetic behaviour of ZnO. The GB character distribution (i.e. GB misorientation and orientation) is different in the textured and non-textured films. Most probably, the GBs with different character possess also different magnetic properties. The role of GBs, free surfaces and interfaces in ferromagnetic behaviour of GaN is discussed. In particular, their presence permits to increase the Mn solubility in GaN without precipitation of secondary ferromagnetic phases.

1 Introduction Dietl et al. have theoretically predicted that ZnO and GaN doped by ‘magnetic’ atoms like Co, Mn or Fe possess ferromagnetic (FM) behaviour with a high Curie temperature $T_c$ above room temperature (RT) [1]. This is due to carrier-related FM interactions, where the FM ordering of the transition metal (TM) ions is induced by a magnetically polarized and doping modified ZnO host. The free carriers can also induce ferromagnetic behaviour [2]. In particular, two distinct ferromagnetic mechanisms in different conductivity regimes can exist. In the insulating regime, carriers tend to be localized, favouring the formation of bound magnetic polarons, which leads to ferromagnetism. In the metallic regime, however, most carriers are weakly localized and the free carrier-mediated exchange is dominant [2]. In order to elucidate the dependence of RT ferromagnetism on the microstructure in ZnO, we have recently analyzed a large series of experimental publications with respect to the present specific grain boundary (GB) area i.e. the ratio of GB area to grain volume $s_{GB}$ [3]. FM only appears, if $s_{GB}$ exceeds a certain threshold value $s_{th}$. Based on this important finding, nano-grained pure and Mn-doped ZnO films have been prepared, which reveal reproducible RT-FM, where the magnetization is proportional to the film thickness, even for pure ZnO films [3]. Our findings strongly suggested that grain boundaries and related vacancies are the intrinsic origin for RT ferromagnetism.

It is very well known for the GBs in metals that the GB character distribution (i.e. GB misorientation and orientation) can drastically change the properties of polycrystals [4, 5]. The goal of this work was to compare the magnetic properties of nanograined ZnO films with the same grain size (well above the threshold value $s_{th}$) but with different
character distribution. Similar to Ref. [3], we also discuss the influence of GBs and interface boundaries on Mn solubility and ferromagnetic behaviour of Mn-doped GaN.

2 Experimental ZnO thin films consisting of dense equiaxial nanograins were produced by using the novel method of liquid ceramics [3, 6-8]. The zinc (II) butanoate diluted in the organic solvent with zinc concentrations between 1 and 4 kg/m³ was used as a precursor for the preparation of ZnO films. The butanoate precursor was deposited on the (102) oriented sapphire single crystals. Thermal pyrolysis at 100 °C in air (about 10 min) was followed by an annealing in an electrical furnace in pure argon (650 °C, 30 min) or in air (550 °C, 24 h). Similar method was recently proposed for zinc oleates [9]. The presence of other magnetic impurities as Fe, Co and Ni was measured by atomic absorption spectroscopy in a Perkin-Elmer spectrometer and electron-probe microanalysis (EPMA). It was below 0.001 at%. The films were transparent and sometimes with a very slight greenish furnish with thicknesses between 50 and 900 nm. The thickness was determined by means of EPMA and edge-on transmission electron microscopy (TEM).

EPMA investigations were carried out in a Tescan Vega TS5130 MM microscope equipped by the LINK energy-dispersive spectrometer produced by Oxford Instruments. TEM investigations were carried out on a Jeol JEM-4000FX microscope at an accelerating voltage of 400 kV. X-ray diffraction (XRD) data were obtained on a Siemens diffractometer (Co Kα1 radiation). Evaluation of the grain or particle size ($D$) from the X-ray peak broadening was performed using Scherrer equation $\beta = 0.9\lambda / D\cos\theta$ where $\lambda$ is the X-ray wavelength, $\theta$ the diffraction angle and $\beta$ is the full-width at half maximum of the diffraction line [10]. The magnetic properties were measured on a superconducting quantum interference device SQUID (Quantum Design MPMS-7 and MPMS-XL). The magnetic field was applied parallel to the sample plane (in plane).

3 Results and discussion Figure 1 shows the dark field TEM micrograph of the nanograined pure ZnO thin film deposited on sapphire and annealed in argon. Electron diffraction pattern (inset) shows only rings from the ZnO wurtzite structure. No texture is visible. The nanocrystalline and dense film of pure ZnO consists of equiaxial grains with a mean grain size of about 20 nm. The grain size in the ZnO films deposited on sapphire and annealed in air is also about 20 nm.

Figure 2 shows the XRD spectra for ZnO thin films deposited on the (102) oriented sapphire single crystals and annealed in air (top) and in argon (bottom). The spectrum for the film annealed in argon (bottom) contains three peaks corresponding to the 100, 002 and 101 reflections of the ZnO with hexagonal wurtzite structure. However, the intensity ratio does not match the standard sample (i.e. powder diffraction pattern taken from a database). The most intense Bragg peak should be 101 for a random distribution which is not the case. It means that the orientation of the nanograins in the ZnO film synthesized in argon is not completely random. The electron diffraction pattern for this film (see inset in the Fig. 1) contains all rings for the hexagonal wurtzite structure, but the bright spots for individual grains are not fully homogeneous distributed along each of the rings. The XRD
polycrystal can also influence the magnetization of
concluded that the topology of the GB network in a
boundaries and related vacancies are the intrinsic origin for
remains diamagnetic. We recently observed that grain

film annealed in air after subtraction substrate diamagnetism.

The film annealed in air clearly shows the pronounced FM
behaviour and remains diamagnetic. In Fig. 3
circles). The full triangles show the magnetization curve
in air is somewhat smaller in comparison with its
counterpart.

Figure 3 contains the magnetization curves for ZnO thin
films annealed in air (full triangles) and in argon (full circles).
The full triangles show the magnetization curve after subtraction of the input of the bare sapphire substrate. The film annealed in air clearly shows the pronounced FM indicated by the saturation of magnetization (above the applied field ~ 6 T). The film annealed in argon does not reveal the FM behaviour and remains diamagnetic. In Fig. 3 the full circles demonstrate the magnetization of ZnO thin film annealed in air after subtraction substrate diamagnetism. Open circles show the magnetization curve for the bare sapphire substrate without diamagnetism. The comparison of the latter curves shows that the ZnO film annealed in argon does not show any additional ferromagnetism with respect to the bare substrate.

The comparison of Figs. 2 and 3 demonstrates that the strongly textured ZnO film possesses the ferromagnetic behaviour and the non-textured (or weakly textured) film remains diamagnetic. We recently observed that grain boundaries and related vacancies are the intrinsic origin for RT ferromagnetism in polycrystals [3]. In Ref. [11] we concluded that the topology of the GB network in a polycrystal can also influence the magnetization of ferromagnetic ZnO films. The GBs in ferromagnetic nanograined ZnO contain the amorphous rather irregular layers [12]. These layers in the Mn-doped ZnO concentrate the ‘magnetic’ impurity Mn [13].

Present results demonstrate that not only the specific area of GBs in nanograined ZnO alone determines the ferromagnetic behaviour of ZnO. We observed here that even when the grain size is well below the critical value for the presence of ferromagnetism for pure ZnO [3], the ferromagnetic behaviour depends on the fact whether the film is textured or not. Similar examples can be found in the literature, namely the nanograined films with specific GB area $s_{GB}$ exceeds a certain threshold value $s_{th}$ remain paramagnetic [13, 17, 20]. It is especially typical for the nanograined ZnO films deposited on the single crystalline sapphire substrates [13, 17, 20]. The same method like pulsed laser deposition [13, 15, 16, 20] or magnetron sputtering [14, 17, 18, 19] allows to manufacture the films with similar grain size but drastically different magnetic properties [13–20]. The GB character distribution (i.e. GB misorientation and orientation) is different in the textured and non-textured films. It is known the GB character distribution can drastically change the properties of polycrystals [4, 5]. Most probably, the GBs with different character in ZnO possess also different magnetic properties.

Dietl et al. predicted in their seminal work on diluted magnetic semiconductors (DMS) that the highest possible Curie temperature could be reached by Mn doping in ZnO and GaN [1]. The magnetization of ZnO depends on Mn concentration very non-monotonously [11]. In the case of GaN, the increase of Mn concentration allows to increase both magnetization and Curie temperature [21–67]. As in ZnO, the Mn concentration in GaN increases up to a certain limit. The addition of Mn above this limit leads to the formation of secondary (ferromagnetic) bulk phases deteriorating the properties of DMS. We observed recently that in case of ZnO the solubility of Mn and Co could be drastically increased without formation of secondary phases by decreasing the grain size of ZnO [6, 7]. XRD measurements demonstrated that the maximal solubility of Mn or Co in the bulk cannot be exceeded, however, the additional atoms of Mn or Co can be absorbed by intergranular, interfacial or superficial layers without formation of secondary phases in the bulk [6, 8, 12]. For example the solubility of Mn in ZnO at 550 °C increases from 12 at% to 33 at% in the films with 20 nm grain size [6]. Is it possible in GaN?

Indeed, the analysis of published experimental data (Fig. 4) shows that the total Mn solubility in GaN also increases with decreasing grain size. The Mn solubility is about 0.2 at% in the perfect bulk GaN single crystals containing only few dislocations [21] and becomes above 18 at% in the thin films obtained by the magnetron sputtering (grain size $d = 15–18$ nm [60]) and ion-assisted deposition (grain size $d = 5$ nm [61, 62]). For ZnO we found that the grain boundaries possess the higher absorbance ability in comparison with free surfaces [6, 8]. In GaN it looks that the free surfaces and interfaces with the substrate play the role
which is comparable with that of GBs. For example, the Mn solubility in the films obtained by CVD reaches at least 2.8 at% [22–29]. The Mn ion implantation into pure GaN CVD-deposited films permits to observe the formation of secondary phase(s) in the Mn-doped GaN samples synthesized by various methods: bulk single crystals grown by the high-pressure method (stars [21]); films produced by the chemical vapour deposition (CVD, diamonds [22–29]) and CVD with following implantation of Mn ions (squares, [30–38]); nanowires (pentagons [39–42]); films produced by the molecular beam epitaxy (MBE, circles [43–60]), magnetron sputtering (MS, up-triangles [61]) and ion-assisted deposition (IAD, down-triangles [62, 63]); micropowders (hexagons [64]); nanopowders (left-triangles [65–67]). Vertical dotted lines mark the maximum Mn solubility for single crystals with diameter $D > 1$ cm (below 2 at%), for the films obtained by CVD or CVD with following implantation of Mn ions (film thickness $h \sim 500$ nm), for the nanowires and films deposited by MBE ($h$ or $D \sim 100$ nm), and for the films manufactured by IAD or MS (columnar grain size $d \sim 100$ nm).

4 Conclusions The structure and magnetic behaviour of pure ZnO thin films deposited by the wet chemistry (‘liquid ceramics’) method from the butanoate precursors on the single-crystalline sapphire substrates depend on the regimes of pyrolysis and following annealing. The films annealed in air ($550^\circ$C, 24 h) have pronounced texture, and they reveal the ferromagnetic behaviour. Argon annealed films ($650^\circ$C, 30 min) have no (or very weak) texture. They remain diamagnetic. Both films have extremely fine (grain size $\sim 20$ nm) grain structure. Present results demonstrate that not only the specific area of GBs in nanograined ZnO alone determines the ferromagnetic behaviour of ZnO. The GB character distribution (i.e. GB misorientation and orientation) is different in the textured and non-textured films. Most probably, the GBs with different character possess also different magnetic properties. The role of GBs in GaN is discussed. In particular, the presence of surfaces and interfaces permits to increase the Mn solubility in GaN without precipitation of secondary ferromagnetic phases.

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