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Microstructure, interdiffusion and magnetic properties of ZnO/MnO_x multilayers grown by pulse laser deposition

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ABSTRACT

ZnO/MnO_x nano-thin multilayers are fabricated by pulsed laser deposition with a sectioned target or "cake" technique. Structure and magnetic properties are measured, finding a magnetic signal that scales better with the number of interfaces than with the film volume, and an interlayer interdiffusion that happens at remarkably low film growth temperatures.

1. Introduction

New and surprising properties such as room temperature ordered magnetism appear at the interphase between ZnO and MnO_2 oxides after partial reaction. There has been some controversy about the origin of magnetism at RT in the ZnO–MnO_x system. The first prediction of the possibility of making magnetic semiconductors [1] which was possible at RT [2] together with the first experimental observation has happened quite recently [3]. We study the possible interfacial origin of magnetism by growing by pulsed laser deposition (PLD) ZnO MnO_x multilayers. It has been claimed that the appearance of magnetism is due to different mechanisms like: diluted magnetic semiconductors [3], secondary phases [4] and to interfacial or superficial phenomena [5–8].

The multilayers are grown by PLD using a target in the shape of a "cake" with two compositions. Detailed investigations looking for the relationship between microstructure, compositional order, quality, interdiffusion and existing phases in the multilayers are performed by high resolution transmission electron microscopy (HR-TEM). Similarly to bulk ceramic oxide mixtures [6,9] it is found that a remarkably low deposition temperature of 400 °C is enough to promote a certain degree of interdiffusion between individual layers and the appearance of room temperature ordered magnetism. It is shown that this magnetic signal scales with the number of interfaces in the multilayer.

2. Experimental

Pulsed laser deposition (PLD), was recognized as a process to deposit metal-oxide films, such as ZnO in the 80s [10], although the first thin film deposition experiments were carried out in 1965 by Smith and Turner [11]. Our home-made PLD system introduces a wedge-target for the deposition of multilayers (see Fig. 1). This target configuration allows the growth of homogeneous thin film (Fig. 1 left) bilayers (Fig. 1 center) and multilayers with individual nanometer thin layers (Fig. 1 right) under the same conditions. The target for multilayers consists of two or more materials and is used for the deposition of complex individual thin layer oxide multilayer structures by PLD. The target structure is similar to a "cake" (see Fig. 1 right) built with portions of different "flavors" that are transferred by PLD to an oxide thin film multilayer. The periodicity of the films is controlled by the laser repetition rate, target rotation speed, and the laser spot energy on the target. Wedge, sectored or split targets have previously been used in PLD processes for depositing monolithic films of variable composition [12–14]. In these cases, the authors used split targets to grow *monolithic films* of $Pb(Zr_{0.48}Ti_{0.52})O_3$ (PZT), $Pb(Mg_{0.33}Nb_{0.66})O_3$–$[PbTiO_3]_x$, and $Ba_xSr_{1-x}TiO_3$ of different compositions by varying the amount of materials ablated from each side of the split targets. They chose conditions that resulted in uniform

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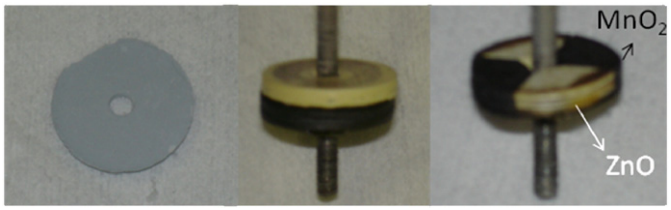

Fig. 1. Three different target configurations used for PLD deposition of thin films, bilayers and thin multilayers. Left, ceramic mixture of ZnO and MnO_2, center: ZnO (top) and MnO_2 (bottom) targets for thick multilayer growth, right "cake" pellet of ZnO and MnO_2 for thin multilayer growth.

compositions throughout the film by growing at relatively slow rates and post-annealing. The systematic shifts in X-ray diffraction measurements of diffraction peak positions show that the conditions used for deposition resulted in monolithic films rather than multilayers. An additional benefit of using the split targets in these experiments was the ability to compensate for the re-sputtering from energetic neutrals and ions from the laser plume [15].

Our thin film multilayers are deposited by pulsed laser deposition on (001) silicon single-crystal substrates [16]. Multilayers are grown by alternating MnO_2 and ZnO ceramic targets prepared by ceramic method and sintered at 500 °C for 12 h. Targets were ablated using a Lambda Physik laser (model LPX 205i MC) operated ($\lambda = 193$ nm) at a pulse repetition rate of 10 Hz, ~150–200 mJ per pulse, a pulse duration of 17 ns, and a target rotation in the range of 1–2 rpm. Multilayers were deposited at an oxygen pressure of 2.10^{-1} mbar and a substrate temperature of 400 °C. Different number of multilayers and bilayer thicknesses were prepared for comparison purposes. The structural characterization of the thin films and multilayers was carried out by XRD analysis in a PHILIPS diffractometer using a Cu K_α line. The thicknesses and uniformity of the films were measured using a Talystep profilometer and Atomic Force Microscopy. Magnetic measurements were carried out over a temperature range of 2.5–300 K on a Quantum Design SQUID magnetometer. When performing the magnetic measurements, all possible sources of spurious signals described in [17] were considered and avoided.

Cross-sectional specimens suitable for transmission electron microscopy (TEM) were prepared by standard procedures: mechanical grinding, dimpling and argon ion milling in a liquid-nitrogen-cooled holder with an acceleration voltage of 5 kV and an incidence angle of 8°. The selected area electron diffraction pattern (SAEDP), energy-dispersive X-ray analysis, TEM and high resolution transmission electron microscopy (HR-TEM) images were carry out using a Philips Tecnai 20F FEG analytical microscope operating at 200 kV equipped with a dark field high angle annular detector (HAAD) for Z-contrast analysis.

3. Results and discussion

Fig. 1 shows the three different target configurations used for PLD deposition. First, a single target: a ceramic mixture of ZnO and MnO_2, second: ZnO (top) and MnO_2 (bottom) targets for thick multilayer growth, and third "cake" pellet of ZnO and MnO_2 for thin layers multilayer growth. These targets are used to grow homogeneous thin films, thick individual multilayer (mostly bilayers) and nanometer thin layer multilayers, respectively. All these target configurations are used to investigate the origin of magnetic signals in oxide mixtures and thin oxide films and heterostructures [5,6].

An example of cross-sectional bright field images oriented along the <110> direction of the Si substrate of a multilayer composed of 26 bilayers ZnO/MnO_x together with dark field HAAD image with compositional Z-contrast is shown on Fig. 2A and B. In this particular case, the multilayers' growth was stopped in the MnO_2 target and a thick layer of MnO_x was grown in between two ZnO layers to confirm

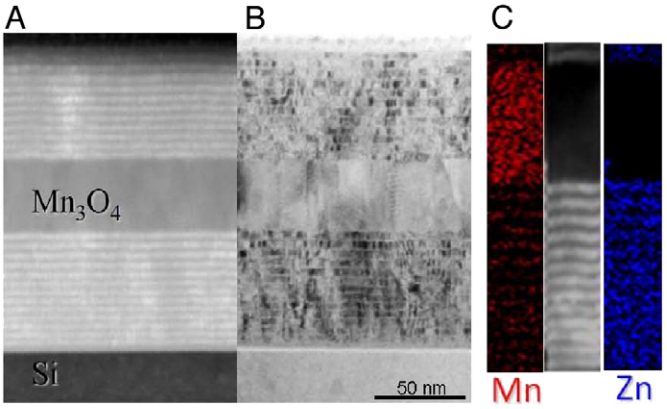

Fig. 2. Cross-sectional images oriented along the <110> direction of the Si substrate. a) STEM dark field Z-contrast image, lighter atoms exhibit darker contrast b) bright field image and c) magnified Z-contrast image at the center and EDX compositional mapping, showing the distribution of Mn and Zn K_α lines.

the Z-contrast and to determine which of the several possible Mn–O phases was growing. The measurements in Å, taken from the SAEDP, in the thick central area of the MnO_x are summarized in Table 1. All the distances measured could be indexed with Mn_3O_4 $a = 3.026$, $b = 9.769$ and $c = 9.568$, JCPDS 750565.

The multilayer is grown on silicon (100) by using a deposition time of 30 s by layer, except the thick Mn_3O_4 layer in the middle that was grown for 9 min. The total thickness measured at the TEM images was 194 nm, in good agreement with the thickness measured by a Talystep profilometer.

The multilayer presents a good morphology with good lateral uniformity, periodicity and with a clear definition of the individual layers. The contrast along the individual layer is associated with their polycrystalline structure, as confirmed by SAEDP and electron nanodiffraction patterns. The roughness of the layers increases with increasing distance from the Si substrate and the maximum roughness measured from HR-TEM images is 3 nm.

The layer thicknesses are in the nanometer range, 5 nm for ZnO and 1.5 nm for MnO_x (around 19 and 5 unit cells, respectively). Since the laser power conditions are the same this means that the deposition rate of ZnO is about 3 times larger than that of MnO_x under these conditions.

To investigate the composition of the layers and the compositional order STEM dark field Z-contrast images have been obtained, see Fig. 2B. Those images indicate a compositional order along the superlattices. In Z-contrast, lighter atoms appear with darker contrast. Compositional mappings were also made after the EDX spectra associated with the STEM images, where the Mn and Zn distribution along the layers is imaged, using the Mn and Zn K_α lines of the EDX spectra respectively. The compositional mappings give a direct

Table 1
Experimental interplanar distances measured when the SAED pattern is taken at the Mn_3O_4 central thick layer.

Interplanars distances measured at the thick central area	Mn_3O_4 $a = 3.026$, $b = 9.769$ and $c = 9.568$, JCPDS 750565
4.87	4.88 (020)
2.84	2.89 (110)
2.68	2.67 (023)
2.75	
2.73	2.76 (111)
1.76	1.76 (142)
1.68	1.70 (044)
1.61	1.61 (151)
1.36	1.358 (231)
	1.372 (230)

indication of the presence of each compound in each multilayer. In this case, the mapping of the thick Mn_3O_4 layer is also shown for clarification. Although the presence of ZnO and Mn_3O_4 layers is clear, a small interdiffusion could be also taking place at the interface.

A magnification of the multilayer structure is shown in Fig. 3. The contrast is defined by the (002) ZnO lattice fringes. Disorder and different thickness are observed at the interfaces indicating a non-regular distribution of the Mn oxide and also observed in the EDX mappings. A columnar growth of the multilayer is also observed. A high resolution TEM image of the ZnO layer is also shown in the inset of Fig. 3B together with the corresponding FFT electron diffraction simulation. According with the distances measured the ZnO (001) axis is perpendicular to the substrate surface.

In order to investigate the individual layer composition and if a diffusion process takes place between the multilayers a low magnification SAEDP was performed. The oriented monocrystalline spot pattern of the (110) Si substrate plane was used as an internal calibration. A typical SAEDP pattern obtained is shown in Fig. 3C, and the main distances obtained from the measurements are summarized and compared with the expected values for the compounds as shown in Table 2. The diffraction patterns consist of hazy rings from the polycrystalline phase and relatively sharp and weaker diffraction spots from individual nanocrystals. With the resolution achieved, the distances corresponding to Mn_3O_4, ZnO and $Zn_xMn_{2+x}O_4$ can be identified. The appearance of the new spinel $Zn_xMn_{2+x}O_4$ phase can only be explained by the intermixing produced between ZnO and Mn_3O_4 layers at 400 °C. So, it can be claimed that multilayers interdiffusion is found at lower temperatures than expected (400 °C) as compared with solid-state methods [8]. Since it is a diffusion controlled process the amount of $Zn_xMn_{2+x}O_4$ will depend on the time that the multilayer is at 400 °C. So an important parameter that should be taken into account to reduce the intermixing of the layers is the total deposition time.

Fig. 4 shows the magnetic signal for two multilayers grown with the same number of individual layers, but with nominally double thicknesses. Both multilayers are composed of 40 bilayers ZnO/Mn_3O_4. The multilayer measured thickness for B187A is 70 nm and 200 nm for B207A. Fig. 4A shows the measured magnetic moment per unit volume, and Fig. 4B shows the measured magnetic moment. Remarkably, both multilayers have similar magnetic moments, but the magnetic moment per unit volume is smaller for the thick multilayer film. This experimental fact points to a magnetic signal that scales with the number of interfaces in the multilayer and not with the film volume. Strongly suggesting an interfacial origin of the room temperature ferromagnetism-like behaviour [5,6].

Summarizing the above experimental data: it turns out that even at low temperature film deposition there is a certain degree of interdiffusion and ordered magnetic properties appear, at the interface between two oxides. One is diamagnetic, ZnO, and the other is paramagnetic Mn_3O_4 in their bulk forms. The thicknesses of

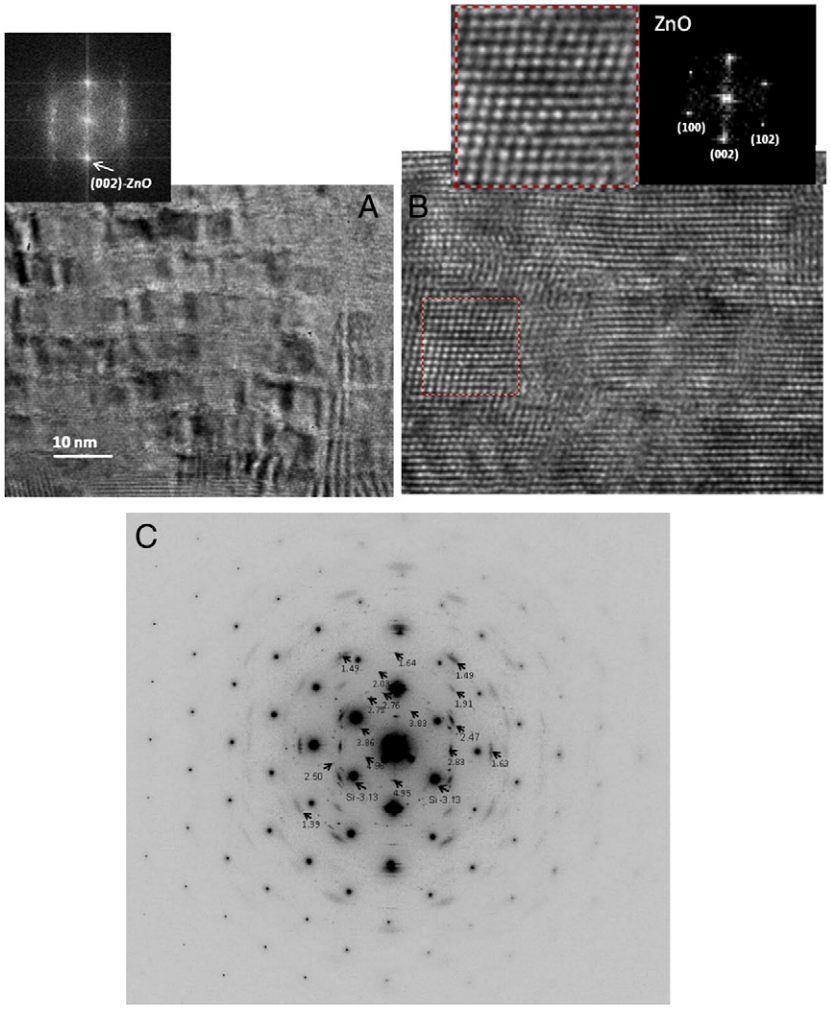

Fig. 3. A) High resolution TEM image of the multilayer and FFT electron diffraction simulation of the multilayers. The contrast is defined by the lattice fringes of (002)-ZnO. B) Higher magnification images, at the inset: selected area and FFT corresponding to (020)-ZnO. C) Selected area diffraction patterns (SADP). The larger black dots, corresponding to more intense diffracted beams represent the (110) Si substrate and are used as an internal calibration. The distances are displayed in Å and are interpreted in Table 1.

Table 2
Summary of the experimental interplanar distances from the ZnO/Mn_3O_4 multilayers compared with the expected values for the compounds present in the multilayers. The (110) Si substrate is used as an internal calibration.

Distances measured in SADP (Å)	Mn_3O_4 (Å) JCPDS = 750765	ZnO (Å) rings JCPDS = 760704	$Zn_xMn_{2+x}O_4$ (Å) JCPDS = 241133
4.87		4.88 (020)	4.87 (101)
4.36		4.35 (021)	
3.85 (Si)			
3.1		3.02 (100)	3.05 (112)
2.86		2.89 (110)	2.86 (200)
2.8	2.81 (100)		
2.79		2.77 (111)	
2.75			2.715 (103)
2.72(Si)			
2.68		2.67 (023)	
2.48	2.48 (121)	2.48(121)	2.47 (112)
		2.47 (211)	
2.3			2.31 (004)
2.03			2.02 (220)
2		2.01 (132)	
1.73			1.76 (105)
1.63	1.63 (110)	1.64 (150)	1.62 (303)
1.6		1.61 (151)	
1.52			1.52 (224)
1.49		1.49 (210)	
1.48	1.48 (103)		
1.45		1.45 (063)	
1.44			1.44 (116)
1.41	1.41 (200)		
1.37	1.38 (112)		
1.37		1.37 (230)	
1.36	1.36 (201)	1.36 (231)	
1.3	1.30 (004)		
1.23	1.24 (202)		
1.2	1.2 (104)		
1.1	1.1 (203)		

the layers are such that ZnO, manganese oxide, and an incipient manganese zinc spinel phase are resolved. It is then concluded that a crucial parameter to be taken into account in order to explain the variety of results of the magnetic measurements in multilayers is the control of the interdiffusion.

In order to confirm this hypothesis, short period multilayer (using 20 s per layer) was grown at 400 °C with the same laser conditions as before. When the multilayers are not thick enough, Fig. 5, a complete interdiffusion occurs during growth at 400 °C in the layers close to the substrate surface. Three different areas can be observed. 1) In the area closest to the substrate surface there is no multilayers pattern, see Fig. 5C. Only a polycrystalline structure is observed, as corroborated by TEM. The SAEDP patterns (not shown), indicate the presence of the mixed oxide ($Zn_xMn_{2+x}O_4$) together with small amount of ZnO and Mn_3O_4 coming from the top layers that did not have enough time to interdiffuse and they are still observed, see Fig. 5B. 2) In the top part of the film a good morphology multilayer of approximately 1.1 nm Mn_3O_4 and 3.9 nm ZnO can be measured, see top part of Fig. 5B. And, 3) in between those two parts (middle of the film) an important interdiffusion is shown, see the bottom part of Fig. 5B. In Fig. 5D a sketch of the diffusion model can be found. In summary, the first multilayers, the one close to the substrate, have already reacted and form the $Zn_xMn_{2+x}O_4$ phase. While in the few top multilayers the diffusion has not yet occur totally and a few of discontinuous multilayers can still be differentiated.

The disappearance of the Mn_3O_4 phase can also be followed by XRD, see Fig. 6. For the thicker multilayers (for deposition time per layer over 30 s) three phases can be detected in the diffraction pattern ZnO, Mn_3O_4 and $Zn_xMn_{2+x}O_4$. While for the thinner multilayers (time of less than 20 s per layer) the Mn_3O_4 diffraction maxima disappear and only ZnO and $Zn_xMn_{2+x}O_4$ could be detected.

Then, in order to control the interdiffusion and to grow good quality multilayers three parameters play an important role (growth temperature, layer thicknesses and total deposition time at high temperature). These facts are also illustrated in Fig. 5, where a multilayer structure is observed only in the top multilayers, while the multilayers close to the substrate have already reacted to form $Zn_xMn_{2+x}O_4$. This happens as the growth of the top multilayers proceeds. If the individual layers are too thin, or the deposition time is too long, or the deposition temperature is too high, interdiffusion takes place and the multilayers react to form a new compound. This is important to define the optimal growth conditions to obtain high quality multilayers.

4. Conclusions

ZnO MnO_2 thin film oxide multilayers are grown by PLD using "cake" targets. The multilayer is made of two oxides, one is diamagnetic, ZnO, and the other is paramagnetic Mn_3O_4 in their bulk forms. The ZnO PLD yield is about 4–5 times that of the MnO_2 target. Our results indicate that the magnetic signal in ZnO–MnO_x oxide multilayers scales with the number of interfaces. Structural studies show that even at very low deposition temperatures (400 °C) an interdiffusion between the ZnO and the MnO_x layers occurs. That eventually can produce an incipient $Zn_xMn_{2+x}O_4$ spinel. Since it is not possible to grow crystalline and good quality the multilayers without a certain temperature, it is very important to optimize the layer thickness, total number of multilayers and the total deposition time, to control or minimize the interdiffusion, in order to obtain good quality interfaces between the two different oxides. Since a non-optimized process will promote the interreaction or interdiffusion between layers and the multilayer will no longer exist. It is then demonstrated that even at temperatures as low as 400 °C

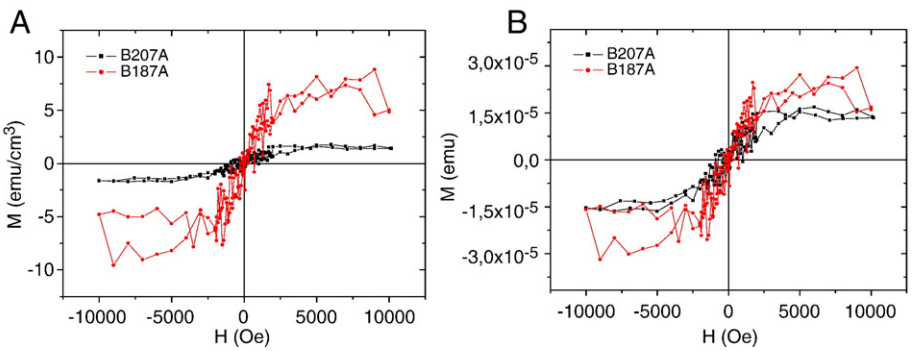

Fig. 4. Magnetic loops for two multilayers grown with the same number of individual layers but with nominally double thicknesses, i.e., double deposition time of the individual layers. Both multilayers are composed of 40 bilayers of ZnO/MnO_x. The multilayer measured thicknesses for B187A is 70 nm and 200 nm for B207A. Panel A shows the measured magnetic moment per unit volume, and panel B shows the measured magnetic moment.

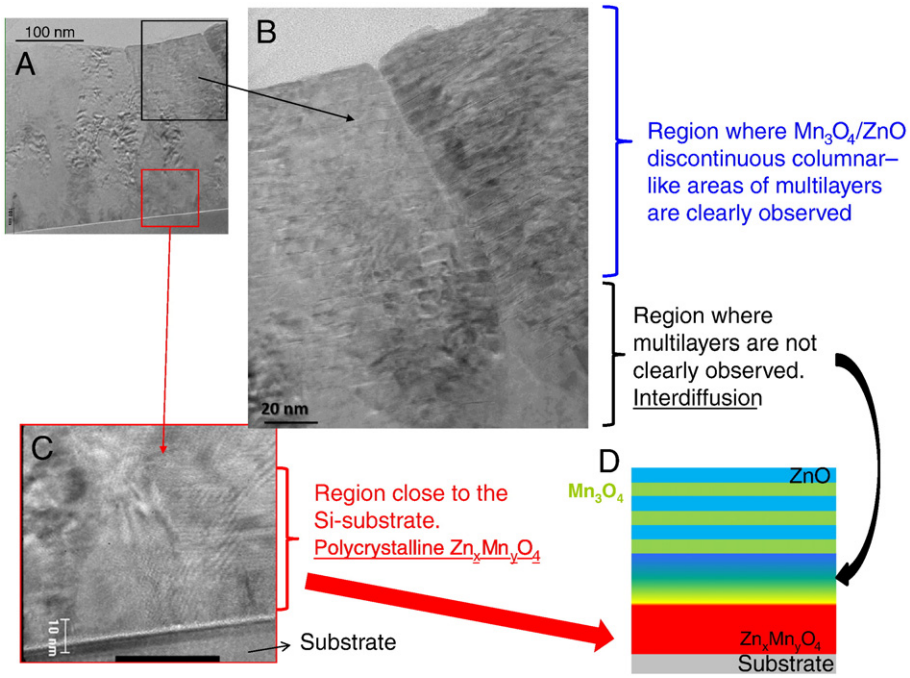

Fig. 5. Interdiffusion model: top left image is a TEM image of the multilayer, with magnifications of the multilayer structure close to the surface (top right) and to the substrate (bottom right). The sketch at the bottom left illustrates the different structures along the growth direction due to different degrees of interlayer diffusion.

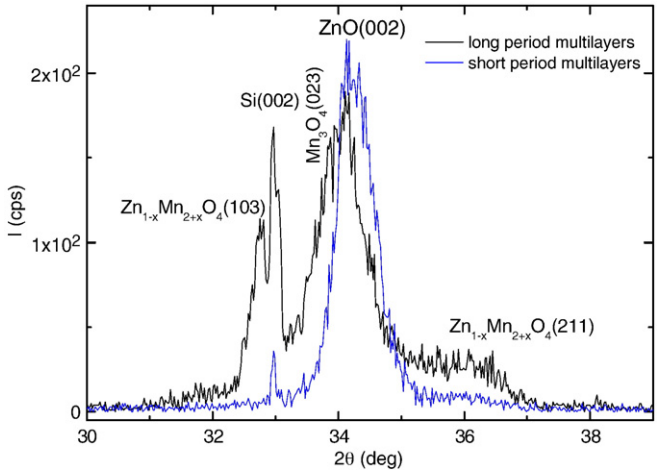

Fig. 6. X-ray diffraction pattern of two samples one with long period multilayers where ZnO, Mn_3O_4 and $Zn_xMn_{2+x}O_4$ can be clearly observed and one short period multilayers where only ZnO and $Zn_xMn_{2+x}O_4$ can be detected. The different diffraction maxima have been indexed.

interreaction occurs, well below the one expected in bulk form. Room temperature magnetic ordered properties appear only when the interdiffusion is controlled and interfaces are present.

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References

[1] H. Ohno, Science 281 (1998) 951.
[2] T. Dietl et al., Science, 287, 1019 (2000).
[3] P. Sharma, et al., Nat. Mater. 2 (2003) 673.
[4] D. Kundaliya, et al., Nat. Mater. 3 (2004) 709.
[5] M.A. García, et al., Phys. Rev. Lett. 94 (2005) 217206.
[6] A. Quesada, J. Appl. Phys. 100 (2006) 113909.
[7] M.S. Martín-González, J. Appl. Phys. 103 (2008) 083905.
[8] J.F. Fernandez, J. Eur. Ceram. Soc. 26 (2006) 3017.
[9] J.L. Costa-Krämer, et al., Nanotechnology 16 (2005) 214.
[10] H. Sankur, J.T. Cheung, J. Vac. Sci. Technol. A 1 (1983) 1806.
[11] H.M. Smith, A.F. Turner, Appl. Opt. 4 (1965) 147.
[12] S.K. Hau, K.H. Wong, P.W. Chan, C.L. Choy, Appl. Phys. Lett. 66 (1995) 245.
[13] W.M. Yu, K.H. Wong, Integr. Ferroelectrics 55 (2003) 947.
[14] V. Ruckenbauer, F.F. Hau, S.G. Lu, K.M. Yeung, C.L. Mak, K.H. Wong, Appl. Phys. A 78 (2004) 1049.
[15] S.K. Hau, K.H. Wong, P.W. Chan, C.L. Choy, Appl. Phys. Lett. 66 (1995) 245.
[16] E. López-Ponce, et al., Jpn. J. Appl. Phys. 45 (2006) 7667.
[17] M.A. García, E. Fernández Pinel, J. de la Venta, A. Quesada, V. Bouzas, J.F. Fernández, J.J. Romero, M.S. Martín González, J.L. Costa-Krämer, J. Appl. Phys. 105 (2009) 013925.