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Magnetism in transition-metal-doped In_2O_3 thin films

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Abstract

Laser ablated transition-metal (TM)-doped In_2O_3 thin films grown under appropriate conditions on both MgO and Al_2O_3 substrates can be well crystallized and ferromagnetic at room temperature. Of all the dopants, Ni seems to be the most promising candidate since doping Ni in In_2O_3 results in semiconducting films with the largest magnetic moment. Films are cluster-free. Magnetic force microscopy measurements confirm that the magnetic signals at room temperature are real. Moreover, compared to TM: In_2O_3 films deposited on MgO, films on Al_2O_3 have smaller grains and those are better connected, so that the film texture is smoother and the magnetic domains are more uniform. The size of ferromagnetic domains is determined to be about $1\ \mu\text{m}$. The room temperature ferromagnetism in V/Cr/Fe/Co/Ni-doped In_2O_3 films probably originates from the doped In_2O_3 matrices.

1. Introduction

Since the theoretical prediction of Dietl that it should be possible to obtain ferromagnetism (FM) in Mn-doped semiconductors [1], diluted magnetic semiconductors (DMS) have attracted a lot of interest due to their potential for spintronic applications. Following this line of research, simulation work by Sato and Katayama-Yoshida pointed out that doping other transition metals (TM) in ZnO could produce high Curie temperature (T_C) FM [2]. Since then, many experimental investigations have been carried out in the hope of finding promising compounds, which are ferromagnetic at room temperature. In this quest, not only have the types of dopants been varied, but also the host oxide. Experiments on TM-doped- TiO_2 , ZnO as well as SnO_2 thin films have suggested that TMs certainly could be exploited to dope in many different semiconductor oxides in order to produce high T_C ferromagnetic materials [3–9]. Since In_2O_3

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is a transparent, wide-band-gap (3.75 eV) semiconductor with a cubic structure, which is rather complicated and somewhat different from the other host oxides that have been studied so far [10–12], it would be a big challenge to achieve FM in this matrix. Up to now, there have been only two reports on the FM in Fe- and Ni-doped In_2O_3 thin films [11, 13]. In this work, we have undertaken a systematic investigation on structural and magnetic properties of V/Cr/Fe/Co/Ni-doped In_2O_3 thin films grown on MgO and Al_2O_3 substrates. The origin of the observed magnetism will be fully clarified.

2. Experiment

TM-doped In_2O_3 films (where TM = V/Cr/Fe/Co/Ni) were grown on (001) MgO and *R*-cut Al_2O_3 substrates using the pulsed laser deposition (PLD) technique (KrF laser, $\lambda = 248$ nm) from $\text{In}_{1.9}\text{TM}_{0.1}\text{O}_3$ (doping 5%) ceramic targets made by the solid-state reaction method. The repetition rate was 10 Hz and the energy density was 2.5 J cm^{-2} . The substrate temperature was kept constant at 550°C . During deposition, the oxygen partial pressure (P_{O_2}) was 10^{-6} Torr, and after deposition, films were cooled down slowly to room temperature under a P_{O_2} of 20 mTorr. The typical thickness of the films is 350 nm. The structural study was done by x-ray diffraction (XRD). The chemical compositions were determined by Rutherford backscattering spectroscopy (RBS) measurements. The magnetic moment (M) was determined by using a Quantum Design superconducting quantum interference device (SQUID) system under magnetic fields (H) from 0 up to 0.5 T applied parallel to the film plane, for a range of temperatures (T) from 400 K down to 5 K. Magnetic force microscopy (MFM) measurements were performed under zero field at room temperature. The magnetic probe was a standard cantilever coated with a magnetic layer of CoCr, and it was magnetized perpendicular to the film plane. The MFM measurements were executed by a two-pass method. In the first pass, the topography was determined and in the second one, the cantilever was lifted to a height, which should be higher than where the Van der Waals forces could exist, and then finally the magnetic signals were recorded. Note that for films on both types of substrates, the same tip and the same lift height (about 55 nm) were applied.

3. Results and discussions

All the films are colourless, shiny and highly transparent. TM: In_2O_3 films are semiconducting at room temperature (resistivity is about $\Omega \text{ cm}$) and the resistance rises quickly as the temperature decreases. All the TM: In_2O_3 films grown on both types of substrates were well crystallized as the In_2O_3 structure (see a typical example for XRD patterns of the Ni: In_2O_3 films in figure 1). Peaks are very sharp, and have a very strong intensity. No peak of any secondary phase can be seen in the spectra (at least from XRD measurements with a detection limit of less than 5%). Films on both MgO and Al_2O_3 are mainly oriented along the [111] direction: one can see that (222) and (444) peaks are much stronger than the (400) peak, indicating that the orientation along the [111] direction is more dominant. It is similar to the case of Fe: In_2O_3 films that He *et al* reported in [11]. On the other hand, it is also found that only for the TM: In_2O_3 films grown on Al_2O_3 , the lattice parameter is exactly the same as that of the non-doped In_2O_3 ($a = 10.11 \text{ \AA}$) [12]. It is likely that in the case of films grown on Al_2O_3 substrates, a solid solution might be obtained. In spite of the difference in types of dopants, the lattice parameters of V/Cr/Fe/Co/Ni: In_2O_3 films are not very different from one other. Also from this very small discrepancy, we must say that the dopants seem to be really substituted for indium in the In_2O_3 host matrix.

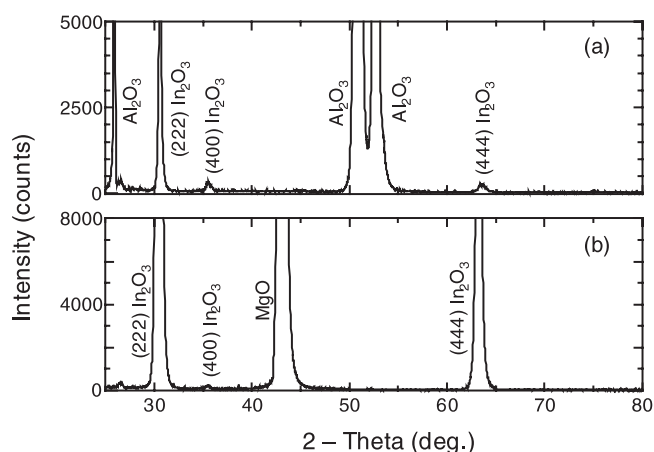


Figure 1. XRD patterns for the Ni: In_2O_3 films grown on (a) Al_2O_3 and (b) MgO substrates.

The dopant content in the TM: In_2O_3 films is determined to be 5%, exactly the same as that in the synthesized targets. Comparing to results on TM-doped TiO_2 or TM-doped ZnO thin films [14, 15], it is found that with the In_2O_3 host, the dopant content does not deviate much from that of the target, and suitable concentrations could be obtained more easily.

RBS spectra show that, except for the Fe: In_2O_3 films, where Fe atoms seem to be located mostly in the upper layer taken from the surface (i.e. having a skin effect, that is similar to the case of Fe: TiO_2 films that has been reported in [16]), for all other cases of TM: In_2O_3 films, indium atoms and V/Cr/Co/Ni atoms were distributed very uniformly over the whole film thickness. Some typical examples for the RBS spectra of the TM: In_2O_3 films are shown in figure 2. One can see that the In peak and the peak of the dopant element are very well separated. The peaks of dopant elements (in figure 2, they are Co and Ni peaks) have a perfect rectangular shape, which is very similar to that of the In peak, showing that the dopant distribution in the TM: In_2O_3 films is largely uniform over the whole thickness of the films. It is completely different from the cases of Co/Ni doped TiO_2 film [14, 16] and Co-doped ZnO film [17], where the dopant atoms were mostly localized in the layer of 40 nm from the surface. In general, as for the In_2O_3 host, there is no difficulty in getting a uniform dopant distribution, in contrast to the case of doping TM for other host oxides such as TiO_2 or ZnO. One must certainly assume that, not only does the nature of the dopant decide whether its distribution is uniform or not, but it must also depend on the nature of the host matrix as well as on the growth conditions, which may greatly influence the magnetic ordering of the host lattice.

Under our chosen range of growth conditions, all of the TM: In_2O_3 films grown on MgO substrates are ferromagnetic above room temperature. $M(T)$ curves taken at 0.5 T in figure 3(a) show that all the films have a T_C above 400 K. Room temperature FM is also confirmed by the magnetization data versus magnetic field taken at 300 K. All the [$M(H)$] curves show a well-defined hysteresis loop (a typical example can be seen in figure 3(b)).

As regards V and Cr doping cases, it is not hard to decide whether the FM in the films stem from dopant metal clusters, because in fact, V and Cr metals themselves are non-magnetic. As for Fe and Co dopings, the saturation magnetization (M_s) is very modest (0.4 and 0.5 μ_B /atom, respectively), which also rules out the assumption that the FM in those films could originate from Fe and Co metal particles/clusters, because for Fe and Co metals, M_s should be 2.2 and 1.7 μ_B , respectively [18]. As for Ni doping, the value of M_s of the Ni: In_2O_3 film is 0.7 μ_B /atom

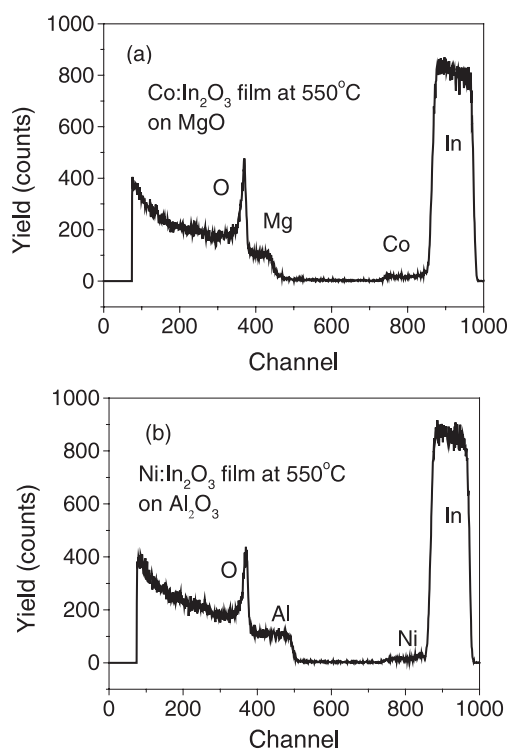


Figure 2. RBS spectra for (a) a Co:In₂O₃ film on MgO and (b) a Ni:In₂O₃ film on Al₂O₃.

which also does not match the value of M_s for Ni metal which is $0.6 \mu_B/\text{atom}$ [18]. Note that to calculate the values of magnetization from magnetic moments, we have used very precise numbers of atoms that were determined strictly from the RBS data, and have assumed that all the dopant atoms contributed to the magnetism of the films.

For the films grown on Al₂O₃ substrates, we also obtained room temperature FM with similar values of M_s , and the maximal magnetic moment that could be obtained is also $0.7 \mu_B$ for the Ni:In₂O₃ films (see figure 4).

The saturation magnetization M_s versus element (where M_s is basically the M value determined at 1 T from $[M(H)]$ curves taken at 300 K) for TM:In₂O₃ films deposited on both types of substrates is summarized in figure 5. One can see that there is almost no difference in M_s for TM:In₂O₃ films grown on MgO and Al₂O₃ substrates. The chemical trend is quite consistent with the theoretical prediction for TM:ZnO single crystals [2], as well with the previous experimental report on TM:TiO₂ films [5]. Compared to the TiO₂ system, the tendency of M_s versus element of the TM:In₂O₃ system is somewhat closer to the simulation for the ZnO system (especially the slope rising up from Fe to Ni). However, at the moment, a reasonable explanation for this can still not be given.

Room temperature FM could be confirmed directly by MFM measurements. The Ni:In₂O₃ films were chosen to be measured because among all the TM-doped In₂O₃ films, Ni:In₂O₃ films have the largest magnetic moment. Therefore, in principle, it should be easier to detect the magnetic signals, and on the other hand, the issue of having clusters or not in the films could be more favourably clarified. Figure 6(a) shows a topography image taken on the area of $2 \times 2 \mu\text{m}^2$ for the Ni:In₂O₃ film on MgO. The corresponding MFM (phase shift) image can be

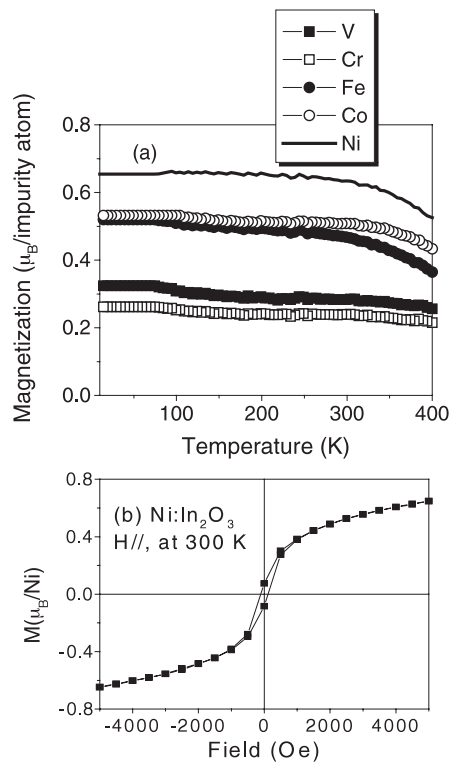


Figure 3. Magnetization (a) versus temperature taken at 0.5 T for TM:In₂O₃ films, and (b) versus magnetic field at 300 K for a Ni:In₂O₃ film grown on MgO substrates.

seen from figure 6(b). The topography image confirms the sample flatness and its low surface roughness of about 2 nm. The asymmetry value on the sample surface within the analysis area (skewness— R_{sk}) is determined to be 0.267. As seen from figure 6, the MFM image is completely different from the topography image (the dark spots seen in figure 6(b) do not match the dark spots seen in figure 6(a)), therefore, the strong signals at room temperature that we have detected, surely come from the magnetic response but not from any surface effect. The real magnetic signals are confirmed by measuring onward and backward. The profiles of the topography and MFM signals recorded on the onward and backward sweepings are shown in figure 6(c). Note that the solid line reflects the height of the topography image, and the dashed line reflects the phase of the MFM image. One can see clearly that a perfect symmetry for all the peaks is obtained. Sweepings back and forth give exactly the same signals that coincide with each other, indicating that the detected signals are real magnetic signal, and any error of measurements is out of the question. From figure 6(a), one can find that for the Ni:In₂O₃ film on MgO, the grains are rather big, and not very uniformly distributed. This remark is confirmed by its profiles in figure 6(c). The density of peaks of both the topography profile and the magnetic phase of the sample is small, showing that the grains are big and not very well connected. This also can be seen from the existence of some fluctuation in the profile for the height of the morphology. The size difference of the observed magnetic domains and the morphologic grains rules out any assumption for the FM that might come from clusters, because if that were the case, one must find a similarity in the MFM profile reflecting the clusters that must expected seen from its corresponding topography image.

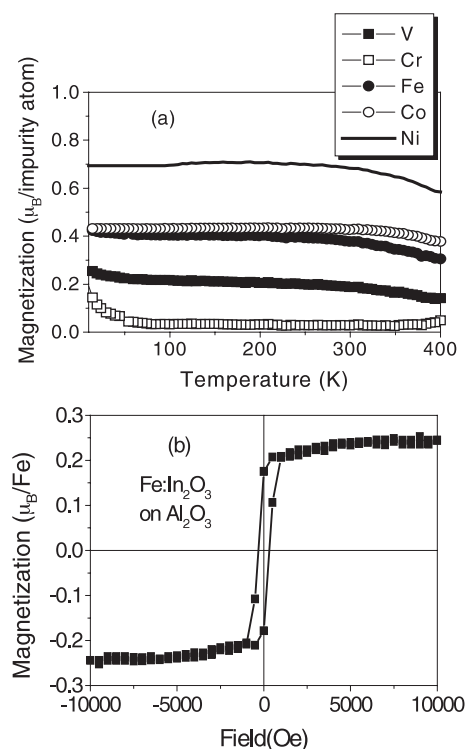


Figure 4. Magnetization (a) versus temperature taken at 0.5 T for TM:In₂O₃ films, and (b) versus magnetic field at 300 K for a Fe:In₂O₃ film grown on Al₂O₃ substrates.

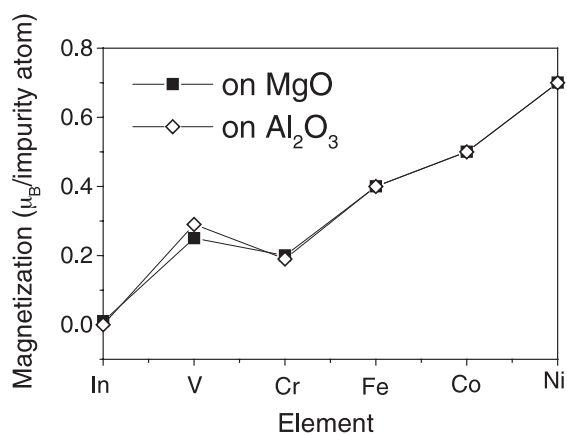


Figure 5. Saturation magnetization versus element for TM:In₂O₃ films grown on MgO and Al₂O₃ substrates (quantitative data taken from the saturated magnetic moments deduced from $[M(H)]$ curves measured at 300 K).

The topography image taken on the same area of $2 \times 2 \mu\text{m}^2$ for the Ni:In₂O₃ film on Al₂O₃, the corresponding MFM images, as well as their profile are shown in figure 7. Note that all the figures/graphs are plotted on the same scale to be able to compare quantitative values directly. The roughness of the film on Al₂O₃ is the same as that of the film on MgO (2 nm). However,

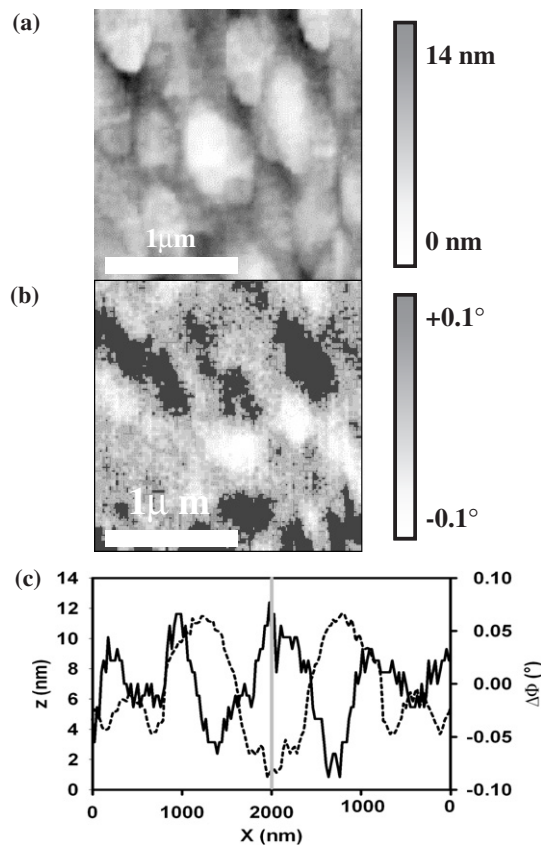


Figure 6. The topography (a), the MFM (b) images and (c) the corresponding profiles of both topography and magnetic signals taken at room temperature on an area of $2 \times 2 \mu\text{m}^2$ of the Ni:In $_2$ O $_3$ film grown on MgO. The tip was magnetized perpendicular to the film plane. Note that in (c), the solid line corresponds to the topography profile and the dashed line corresponds to the magnetic phase profile. Signals were recorded on both onward and backward sweepings. The vertical line at the centre (point at 2 μm) is to distinguish the coordinate border between two sweepings.

the skewness is found to be only a half, indicating a much smoother surface for films on Al_2O_3 . By comparing with figure 6(a), from figure 7(a), one must say that in films on Al_2O_3 , the grains are much smaller, better connected, and are distributed much more uniformly, compared with grains of films on MgO. This is also confirmed by the curve of the topography profile with denser peaks and fewer fluctuations that could be seen from figure 7(c). The magnetic signals detected (figure 7(b)) are real signals and not due to any limitation of the grains due to the morphology effect. Note that the size of the observed magnetic domains in figure 7(b) is completely different from the grain size that could be seen from figure 7(a) (in fact much larger). This is also confirmed by the high coincidence of peaks of the magnetic phase of the sample that were detected on the onward and the backward sweepings: from figure 7(c), one can see a very good symmetry if one considers the point of going back as a reflecting mirror. By comparing figures 7(b) and 6(b), one must find that the magnetic phase of the Ni:In $_2$ O $_3$ film on Al_2O_3 is also much more homogeneous compared to that of the Ni:In $_2$ O $_3$ film on MgO. Such a magnetic homogeneity can be seen not only from a more uniform distribution of the magnetic domains, a much better and more even contrast, but also from the very dense peaks that were

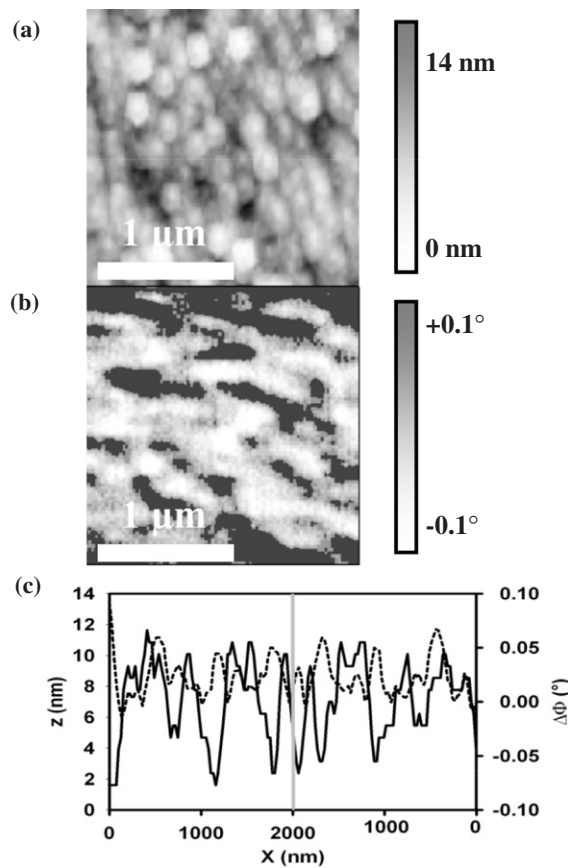


Figure 7. The topography (a), the MFM (b) images and (c) the corresponding profiles of both topography and magnetic signals taken at room temperature on an area of $2 \times 2 \mu\text{m}^2$ of the Ni:In₂O₃ film grown on Al₂O₃. The tip was magnetized perpendicular to the film plane. Note that in (c), the solid line corresponds to the topography profile and the dashed line corresponds to the magnetic phase profile. Signals were recorded on both onward and backward sweepings. The vertical line at the centre (point at $2 \mu\text{m}$) is to distinguish the coordinate border between two sweepings.

revealed from its profile (figure 7(c)). The size of the ferromagnetic domain is determined to be about $1 \mu\text{m}$. As we can clearly see, the difference in the magnetism of films on two types of substrates can be distinguished from a microscopic viewpoint (MFM measurements) but not from a macroscopic viewpoint (SQUID measurements—as discussed in the paragraph concerning figure 5).

4. Conclusions

Transition-metal elements have been used to substitute partially for In in In₂O₃. Laser ablated V/Cr/Fe/Co/Ni-doped In₂O₃ thin films grown on both MgO and Al₂O₃ substrates are well crystallized and ferromagnetic beyond room temperature. The trend of magnetic moment versus element appeared to be consistent with the theoretical predictions. Among all the doped In₂O₃ films, Ni:In₂O₃ films have the largest magnetic moment. Films are probably cluster-free. Besides confirming the magnetic signals at room temperature, magnetic

force microscopy measurements also showed that in comparison to TM:In₂O₃ films on MgO substrates, TM:In₂O₃ films fabricated under the same conditions on Al₂O₃ substrates have smaller, better-connected grains, and as a result the films are flatter and the magnetic domains are more uniformly distributed. The domain size is determined to be about 1 μm. The room temperature FM in V/Cr/Fe/Co/Ni-doped In₂O₃ films probably stems from the doped In₂O₃ matrices.

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