Room temperature ferromagnetism in laser ablated Ni-doped In_2O_3 thin films

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Ni-doped In_2O_3 thin films were fabricated by laser ablation on sapphire and MgO substrates under various conditions. All $Ni:In_2O_3$ films are well-crystallized, single phase, and show clear evidences of room temperature ferromagnetism (FM). Ni atoms were well substituted for In atoms, and distributed very uniformly over the whole thickness of the films. However, the films grown at 550 °C have the Ni concentration exactly the same as in the synthesized target, and as the results, they have the best crystallinity and the largest magnetic moment (maximum about 0.7 μ_B/Ni). The observed FM in this type of wide-band gap semiconductors has proved that by applying appropriate growth conditions, doping few percent of Ni into In_2O_3 could indeed result in a potential magnetic material. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2041822]

Diluted magnetic semiconductors have been attracted a lot of interest due to their great potential for applications in spintronics. Many promising compounds have been found to show room temperature ferromagnetism (FM). Among those, transition-metal (TM)-doped semiconductor oxide thin films appear to be rather good candidates, since they might be produced easily in a controllable way. Experimental studies on TM-doped-TiO_2, ZnO, as well as SnO_2 have suggested that transition metals certainly could be exploited to dope in many host semiconductor oxides in order to result in ferromagnetic materials.[1–9] Since In_2O_3 is a transparent, wide-band gap (3.75 eV) semiconductor with a cubic structure, which is rather complicated and different from the other host matrices that we have dealt with so far,[10] but has been widely used in semiconductor industries,[11] it should be a good challenge to achieve FM in this compound. Moreover, its cubic structure may enable us to use some types of low-cost substrates such as MgO that should be interesting to applications. Up to now, there has been only one report on the FM in Fe-doped In_2O_3 thin films.[11] In this work, we carried out a search for room temperature FM in Ni-doped In_2O_3 thin films grown on different types of substrates.

Ni-doped In_2O_3 films were grown on (001) MgO and *R*-cut Al_2O_3 substrate by using the pulsed laser deposition (PLD) technique (KrF laser, $\lambda = 248$ nm) from an $In_{0.19}Ni_{0.01}O_3$ ceramic target 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 temperatures were 650, 600, or 550 °C. During deposition, the oxygen partial pressure (P_{O_2}) was kept as 10^{-6} Torr, and after deposition, films were cooled down slowly to room temperature under a P_{O_2} of 20 mTorr. The thickness of the films is in the range of 350–630 nm depending on different substrate temperatures. The structural study was done by x-ray diffraction (XRD). The chemical compositions were determined by a Rutherford backscattering spectroscope (RBS). The magnetization measurements were performed by a Quantum Design superconducting quantum interference device system from 0 up to 0.5 T under a range of temperatures from 400 down to 5 K.

All $Ni:In_2O_3$ films on both types of substrate are very shiny and highly transparent. At room temperature, $Ni:In_2O_3$ films are semiconductors with the typical resistivity of about Ω cm and it rises up quickly as the temperature increases. Films on both types substrates were well crystallized as In_2O_3 structure (see very sharp, and strong-intensity peaks in the XRD patterns in Fig. 1). No peak of any secondary phase was seen in the spectra. For films on MgO, films are mainly oriented along the [111] direction. However, when the substrate temperature was increased, the orientation along [100] direction also becomes more apparent (comparing Figs. 1(a) and 1(b) for films fabricated on MgO at 550 and 650 °C, respectively). For films on Al_2O_3, one can see that the (222) and (444) peaks reflecting the orientation along [111] direction are much stronger than the (400) peak, indicating that the orientation along [111] is really dominant. It is similar to the case of $Fe:In_2O_3$ films that He *et al.* reported in Ref. 11. While changing the growth conditions, it is found that lattice parameters do not change much (*a* in the range between 10.11 and 10.17Å). However, one should notice that for $Ni:In_2O_3$ films that were grown at 550 °C on Al_2O_3, the lattice parameter is exactly the same as of the nondoped In_2O_3 ($a = 10.11$ Å). It is most likely that in this case, a solid solution has been obtained.

Ni content was determined by RBS measurements to be 6.8%, 5.3%, and 5.3% for films deposited on MgO at 650, 600, and 550 °C, and 7.8%, 5.5%, and 5% for films grown on Al_2O_3 at 650, 600, and 550 °C, respectively. Since our films were deposited from the target of 5% Ni doping, it

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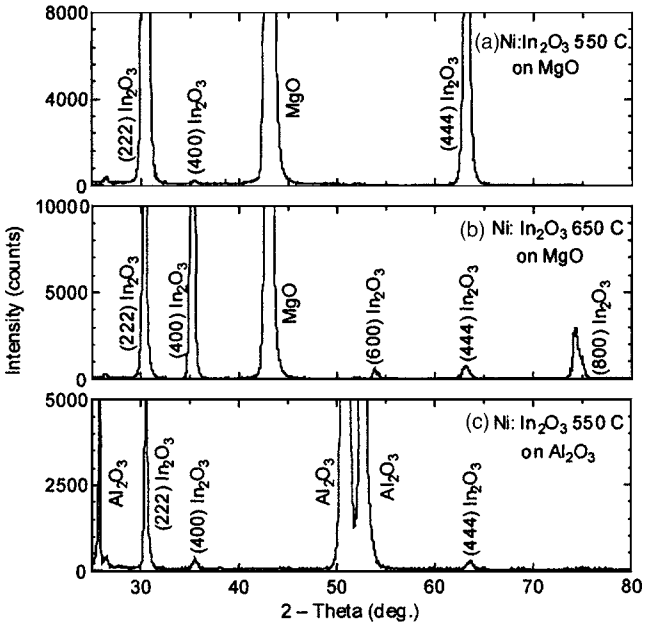

FIG. 1. XRD patterns for $Ni:In_2O_3$ films (a) deposited on MgO at 550 °C, (b) deposited on MgO at 650 °C, and (c) deposited on Al_2O_3 at 550 °C.

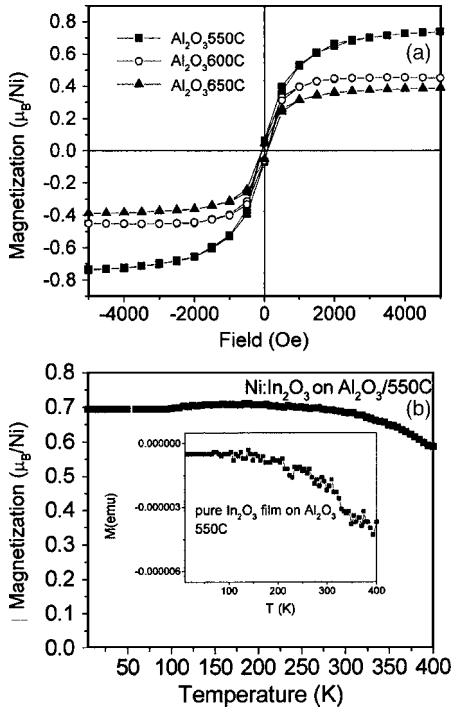

FIG. 3. Magnetization (a) vs magnetic field at 300 K for the $Ni:In_2O_3$ films fabricates on Al_2O_3 at various temperatures and (b) vs temperature at 0.5 T for the $Ni:In_2O_3$ film fabricated on Al_2O_3 at 550 °C. The inset shows $M(T)$ curve at 0.5 T for a nondoped In_2O_3 film grown at 550 °C on Al_2O_3 with the same size and the same thickness as those of the $Ni:In_2O_3$ film whose data are shown in Fig. 3(b).

shows that the dopant concentration in the film could be the same as in the synthesized target if the substrate temperature was 550 °C. It seems that as regards to In_2O_3, a lower temperature likely favors a better solubility. Comparing to TM-doped TiO_2 or TM-doped ZnO thin films,[12,13] it is found that concerning the In_2O_3 host, the dopant content in the films does not deviate so much from that of the target, and it is rather easy to achieve the expected concentration.

RBS spectra showed that both In atoms and Ni atoms are distributed very uniformly in the films. One can see clearly from Fig. 2, the peaks of In and Ni are very well separated, indicating that the determinations of In and Ni contents in the films could be very precise (on the contrary, if there is some overlapping, it should not be possible to say definitely about the number of atoms of each element). The Ni peak has a perfect rectangular shape, which is completely similar to that of the In peak (see more clearly in the inset showing their zoom-up picture in log scale), showing that the Ni distribution in the $Ni:In_2O_3$ films is greatly uniform over their whole thickness. It is completely different from the cases of Co/Fe/Ni doped TiO_2 film[12,14] and Co-doped ZnO film,[15] where the dopant atoms were mostly localized in the layer of 40 nm near the surface as some kind of the "skin" effect. The case of $Ni:In_2O_3$ shows that, compared to Co, Ni is not any more difficultly to be dissolved into the host matrix. It is different from the report of Jin *et al.* saying that Cr, Mn, Fe, and Co are the most soluble among all the elements of the transition-metal group.[16] Thus, we must say that not only does the nature of 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 influence very much the ordering in the host lattice.

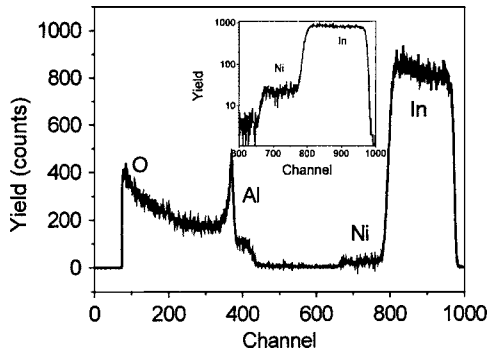

FIG. 2. RBS data for a $Ni:In_2O_3$ film deposited on Al_2O_3 at 650 °C. The inset shows a zoom-up for the Ni and In peaks.

Magnetization data for films on Al_2O_3 are shown in Fig. 3. Films grown at different temperatures all are ferromagnetic at room temperature with T_C well above 400 K [see a typical M-T curve in Fig. 3(b)]. The room temperature FM is confirmed by well-defined hysteresis loops, which were shown in Fig. 3(a). It appears that films grown at a lower temperature could result in a larger magnetic moment. By recalling all the special remarks about the case of films deposited at 550 °C on Al_2O_3: the good crystallinity, the solid solution, and the perfect dopant content that is the same as that of the target, we would see clearly a strong correlation between structural and magnetic properties in here. Obviously, this sample is also most strongly ferromagnetic, with a rather large magnetic moment of about 0.7 μ_B/Ni. (Note that to calculate the values of magnetization from magnetic moments, we used very precise numbers of atoms that was determined strictly from RBS data, by supposing that all the Ni atoms contributed to the magnetism of the films.) Also note that films of nondoped In_2O_3 (with the same thickness) grown on the same size of the same type of substrates under the same conditions are not ferromagnetic [see an example in the inset of Fig. 3(b)]. It rules out completely any assumption for the FM that might be caused by some unintentional contamination of the substrate. The characteristics concerning a relationship between the solid solution and the magnetism

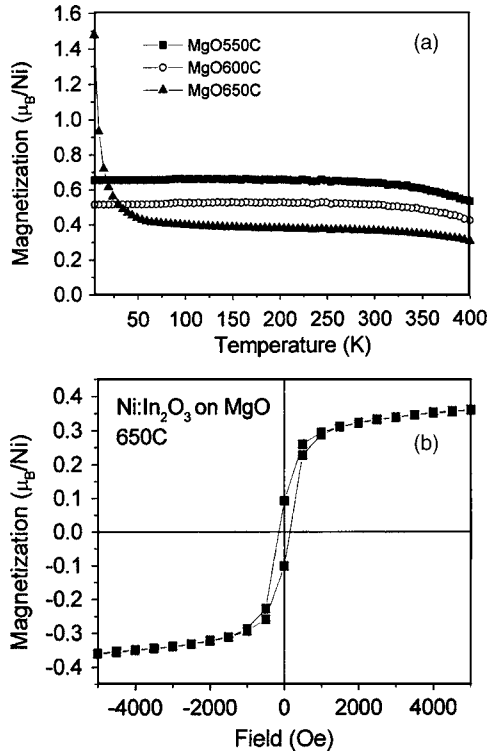

FIG. 4. Magnetization (a) vs temperature at 0.5 T for the Ni:In_2O_3 films fabricates on MgO at various temperatures and (b) vs magnetic field at 300 K for the Ni:In_2O_3 film fabricated on MgO at 650 °C.

that we observed in Ni:In_2O_3 films on Al_2O_3 is very similar to that of Ni:TiO_2 films on $LaAlO_3$ substrates and of Ni:SnO_2 films on $LaAlO_3$, while it is not clearly so in others cases.[17,18] The feature of having a solid solution, which must be strongly related to the resulted magnetism, is likely very common for the type of Ni doping.

Films grown on MgO substrates at various conditions all are also ferromagnetic above room temperature (see Fig. 4). A typical *M-H* curve taken at 300 K is shown in Fig. 4(b) showing that Ni:In_2O_3 films on MgO are certainly room temperature ferromagnets. The *M-T* curves in Fig. 4(a) give the similar remark to those for films on Al_2O_3: all films are ferromagnetic with high T_C (higher than 400 K) and M_s in the range between 0.4 and 0.7 μ_B/Ni, however, films grown at 550 °C seem to have the largest magnetic moment. One point that should be noticed in here is that, there is a rise at the low temperature region of the *M-T* curve of the film grown at 650 °C. Most probably in this case, there might be some precipitations and it could be the reason to reduce the magnetic moment. It is similar to the reports of Xie and Blackman concerning Co clusters,[19] and Hong *et al.* concerning precipitations in of Cr-doped SnO_2 films.[7] It might also be related to the structural data that were shown earlier for this sample is that the (100) orientation is very prominent (different from films grown at lower temperatures), and the Ni content is also deviated rather much from that of the target.

In conclusion, room temperature ferromagnetism could be well obtained in Ni-doped In_2O_3 thin films grown by PLD on sapphire and MgO substrates. Under various conditions, ferromagnetic Ni:In_2O_3 films were well crystallized as the In_2O_3 structure with no trace of any secondary phase. Moreover, Ni atoms were most probably substituted for In atoms, and their distribution in the host matrix is greatly uniform. Films grown at a rather low temperature as of 550 °C have the Ni concentration exactly the same as that in the synthesized target, and simultaneously have the best crystallinity and the largest magnetic moment (about 0.7 μ_B/Ni). Most likely in this case, a solid solution was obtained. On the contrary, increasing the substrate temperature of 100 °C might cause a reduction in magnetic moments due to a probable coexistence of some antiferromagnetic precipitations. This work has proved that by applying appropriate growth conditions, doping a few percent of magnetic ions such as Ni could indeed produce high T_C ferromagnetism in the wide-band gap In_2O_3 semiconductor.

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