Six-fold in-plane magnetic anisotropy in Co-implanted ZnO (0001)

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Magnetic anisotropies of Co-implanted ZnO (0001) films grown on single-crystalline Al$_2$O$_3$ (1120) substrates have been studied by ferromagnetic resonance (FMR) technique for different cobalt implantation doses. The FMR data show that the easy and hard axes have a periodicity of 60° in the film plane, in agreement with the hexagonal structure of the ZnO films. This six-fold in-plane magnetic anisotropy, which is observed for the first time in ZnO-based diluted magnetic semiconductors, is attributed to the substitution of cobalt on Zn sites in the ZnO structure, and a clear indication for long range ferromagnetic ordering between substitutional cobalt ions in the single-crystalline ZnO films.

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The transition metal (TM)-doped ZnO has attracted a significant amount of interest as a potential oxide-based diluted magnetic semiconductor (DMS) material for implementation in novel spintronic devices. After theoretical predictions of room temperature ferromagnetism in TM-doped ZnO, a number of experimental works on these systems has been done. Actually, some of these studies indeed claim ferromagnetic signals above room temperature. However, the main unresolved question is whether the observed ferromagnetism originates from uniformly distributed TM elements in the ZnO host matrix or whether it is due to the precipitation of metallic ferromagnetic clusters. Recently, we have reported that the implantation of cobalt ions into the nonmagnetic ZnO film causes

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intrinsic ferromagnetism at room temperature and simultaneously creates $n$-type charge carriers without additional doping \cite{16, 17}. We have observed magnetic dichroism at the Co $L_{2,3}$ and O $K$ edges at room temperature as well as the multiplet structure in x-ray absorption spectra around the Co $L_3$ edge, that supports the intrinsic nature of the observed ferromagnetism in Co-implanted ZnO films. Furthermore, we have found that the magnetic moment per substituted cobalt in ZnO is about $2.81 \mu_B$ which is very close to the theoretical expected value of $3 \mu_B/Co$ for Co$^{2+}$ in its high spin state.

In this letter, we report on the six-fold in-plane magnetic anisotropy in the Co-implanted ZnO films, observed for the first time by room-temperature FMR technique. The ZnO (0001) thin films were grown on sapphire (1120) substrates by RF (13.56 MHz) sputtering of a ZnO target \cite{18}. After post-growth annealing, the ZnO samples were implanted with 40 keV Co$^+$ ions to the implantation doses in the range of $0.25 - 2.00 \times 10^{17} ions \cdot cm^{-2}$. More details on growth, structural, electronic and magnetic properties were published elsewhere \cite{16, 17}.

FMR measurements were carried out using a commercial Bruker EMX electron spin resonance (ESR) spectrometer operating in X-Band (9.8 GHz) at room temperature. Angular dependencies of FMR spectra have been recorded with the static magnetic field rotated either in the plane of the samples (in-plane geometry - $\theta=90^\circ$, $\varphi$-varied) or rotated from the sample plane to the normal (out-of-plane geometry - $\theta$-varied, $\varphi$-fixed). The used coordinate axes and relative orientation of applied external magnetic field ($H$) and magnetization vector ($M$) are illustrated in Fig. 1.

![FIG. 1: The coordinate system for FMR measurements of Co-implanted ZnO films.](image-url)
In Fig. 2 we present in-plane FMR spectra of Co-implanted ZnO films and angular dependence of the in-plane resonance fields at room temperature for different implantation doses. The resonance field exhibits oscillatory behavior as a function of the azimuthal angle. The maximum and minimum values of the resonance fields correspond to the hard and easy directions for the magnetization, respectively. The periodicity of the easy and hard axes depends on the implantation dose. As seen in Fig. 2 at implantation doses lower than $0.75 \times 10^{17}$ ions $\cdot$ cm$^{-2}$, the FMR signal is very weak. For the dose of $0.75 \times 10^{17}$ ions $\cdot$ cm$^{-2}$, the FMR signal is pronounced and a two-fold in-plane magnetic anisotropy is observed with a very small contribution from a six-fold anisotropy. The two-fold in-plane magnetic anisotropy is related to cobalt nanoparticles forming a cobalt rich layer in the sapphire substrate, close to the ZnO/Al$_2$O$_3$ interface. Indeed, when the crystalline Al$_2$O$_3$ is implanted with cobalt ions, Co nanoparticles with the hexagonal structure are aligned with their c-axis parallel to the c-axis of the host sapphire. Thus, the Al$_2$O$_3$ matrix provides a magnetic anisotropy to cobalt nanoclusters. In our case, the c-axis of the host Al$_2$O$_3$ is in the sample plane. Therefore, we infer that the two-fold in-plane magnetic anisotropy results from cobalt nanoparticles in agreement with previous studies. For the dose range of $1.00 - 1.50 \times 10^{17}$ ions $\cdot$ cm$^{-2}$, the corresponding FMR data show that the easy and hard axes have a periodicity of 60° in the film plane, in agreement with the hexagonal
structure of the ZnO films. This six-fold in-plane magnetic anisotropy is attributed to the substitution of cobalt on Zn sites in the ZnO layer and it is a clear indication for long range ferromagnetic ordering between substituational magnetic cobalt ions in the ZnO crystal structure. At the highest implantation dose of $2.00 \times 10^{17} \text{ions} \cdot \text{cm}^{-2}$, a two-fold in-plane magnetic anisotropy appears again. This means that for the highest dose, not only substituted cobalt ions but also metallic cobalt clusters are present in the ZnO layer, in accordance with the results published in Ref. [17].

Thus, for the highest implantation dose the resonance signal is ascribed to an overall response of the metal cobalt nanoparticles in both the ZnO layer and the sapphire substrate. In this respect, a gradual decrease of the magnitude of six-fold anisotropy for the dose of $1.5 \times 10^{17} \text{ions/cm}^2$ is noteworthy. Therefore, one can expect the formation of very small cobalt clusters in ZnO layer below the dose of $2.00 \times 10^{17} \text{ions/cm}^2$. Thus, the maximum amplitude of the six-fold anisotropy, revealed at the dose of $1.00 \times 10^{17} \text{ions/cm}^2$, reflects the limit where the highest concentration for the substituional cobalt phase in ZnO is reached. For higher doses, formation of the extrinsic ferromagnetic phase due to Co clusters starts.

FIG. 3: Out-of-plane FMR spectra (a), and the resonance field of FMR signal as a function of polar angle (b), for different cobalt implantation doses
Out-of-plane FMR spectra and the FMR resonance fields as a function of polar angle ($\theta$) are shown in Fig. 3 for different cobalt implantation doses. At low doses the resonance signal is very weak. Increase of the implantation dose results in appearance of the FMR signal, characterized by the six-fold in-plane magnetic anisotropy and attributed to the substitutional cobalt phase in the ZnO layer. In the out-of-plane geometry, this signal consists of a single line for the parallel orientation and two lines for the perpendicular orientation of the ZnO film with respect to the dc magnetic field. The splitting of this signal into two modes is related to the non-homogeneous profile of the cobalt concentration across the film thickness. It is well known that in systems where a gradient of the magnetization as well as a difference in the surface/interface anisotropies exists, non-uniform FMR modes could be observed [21, 22]. Therefore, the splitting into two modes, observed in the perpendicular orientation, is explained by excitation of the surface/interface located modes (at lower field/higher fields, respectively). It should be noted that in the dose range of $1.00 - 1.50 \times 10^{17}$ ions/cm$^2$, where the six-fold anisotropy dominates, the resonance fields and intensity of the low-field mode change only slightly, while the intensity of the high-field mode gradually increases. The latter reflects increased influence of the cobalt metal nanoparticles on the overall FMR signal upon increasing the implantation dose. A strong FMR signal with high effective magnetization, observed at the highest implantation dose of $2.00 \times 10^{17}$ ions · cm$^{-2}$, corresponds to the formation of the percolated layer of the metal Co nanoparticles in the ZnO layer.

In order to check whether the contribution to the six-fold in-plane magnetic anisotropy originates from ZnO only, we gradually removed the ZnO layer by 500 eV Ar-beam etching and repeated the FMR measurements. Fig. 4 presents the in-plane magnetic anisotropies of Co-implanted ZnO film (Co dose: $1.00 \times 10^{17}$ ions · cm$^{-2}$) before and after etching process. When the ZnO layer is etched by about 10 nm, the six-fold symmetry of the in-plane magnetic anisotropy survives, but with a significant decrease in the magnitude of anisotropy. Besides, the signal intensity also gradually decreases with etching. For the completely etched sample the signal with six-fold symmetry completely disappears. This observation shows that the FMR signal with the six-fold in-plane magnetic anisotropy originates from the substituted cobalt in the ZnO film, but not from the cobalt nanoparticles in the Al$_2$O$_3$ substrate.

In conclusion, the magnetic anisotropies of the Co-implanted ZnO films have been investigated by ferromagnetic resonance technique. The six-fold in-plane magnetic anisotropy of the FMR signal has been observed for the first time in ZnO (0001) thin films implanted by Co in the dose range of $1.00 - 1.50 \times 10^{17}$ ions/cm$^2$. This signal is attributed to the ferromagnetic phase formed due to long-range ordering of substitutional cobalt ions in the ZnO host matrix. We consider this finding as a strong indication for intrinsic ferromagnetism in ZnO-based diluted magnetic semiconductors.
FIG. 4: (a) In-plane magnetic anisotropy of Co-implanted ZnO film (Co dose: $1.00 \times 10^{17}$ ions $\cdot$ cm$^{-2}$) before (closed symbols) and after (open symbols) etching. (b) Angular dependence of out of plane spectra taken before (closed symbols) and after (open symbols) etching for the same sample.

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