Optical and magnetic properties of nitrogen ion implanted MgO single crystal*

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(Received 25 September 2010; revised manuscript received 8 December 2010)

The microstructure, optical property and magnetism of nitrogen ion implanted single MgO crystals are studied. A parallel investigation is also performed in an iron ion implanted single MgO sample as a reference. Large structural, optical and magnetic differences are obtained between the nitrogen and iron implanted samples. Room temperature ferromagnetism with a fairly large coercivity field of 300 Oe (1 Oe=79.5775 A/m), a remanence of 38% and a slightly changed optical absorption is obtained in the sample implanted using nitrogen with a dose of 1×10^{18} ions/cm^2. Transition metal contamination and defects induced magnetism can be excluded when compared with those of the iron ion implanted sample, and the nitrogen doping is considered to be the main origin of ferromagnetism.

Keywords: nitrogen implanted MgO, magnetism, optical property, microstructure

PACS: 75.50.–y, 78.20.–e **DOI:** 10.1088/1674-1056/20/4/047505

1. Introduction

Since the experimental study of d^0 magnets in undoped HfO_2,[1] increasing attention has been paid to this field. The term "d^0 magnets" refers to a class of materials that lack any magnetic ions with open d or f shells. Numerous theoretical and experimental papers have proposed that Mg vacancies can induce room temperature ferromagnetism in MgO.[2−5] However, a recent calculation based on the scheme of local spin density approximation (LSDA) + Coulomb interaction (U) provided a number of constraints to the possibility of ferromagnetism induced by Mg vacancies in MgO.[6] Furthermore, it was indicated that a semi-local exchange correlation function, such as the LSDA, incorrectly predicts a delocalized degenerate ground state. Introducing the strong correlation effects by means of the LSDA+U scheme, Liu *et al.*[7] investigated the electronic properties of MgO doped with group III, IV and V elements. They found that all of the geometry optimized systems with the group V elements replacing O in MgO exhibit half metallic ferromagnetic properties. The spin polarized state of nitrogen replacing O in MgO is the most stable one[7]. Using the quantum Monte Carlo technique, Gu *et al.*[8] also reported a finite local moment for an N impurity, and long-range ferromagnetic correlations between two N impurities. To our knowledge, there are few experimental works on the magnetism of nitrogen-doped MgO. One experimental paper reported that the formation of the defects necessary for magnetization is strongly inhibited in nitrogen-doped MgO.[9] Intrigued by this work, in this paper we investigate the magnetic property of MgO implanted with nitrogen. It is found that MgO implanted using nitrogen ions has room temperature ferromagnetism with a fairly large coercivity field of 300 Oe (1 Oe=79.5775 A/m). Compared with the magnetism of iron implanted MgO, the room temperature ferromagnetism of nitrogen implanted MgO should be an intrinsic property.

2. Experiments

The single crystal MgO substrates were obtained from Hefei Kejing Materials Technology Co. Ltd. The nitrogen implantation was performed at an energy of 60 keV in a vacuum chamber of 2×10^{-3} Pa., with the nominal dose varying from 1×10^{16}, 1×10^{17} to

*Project supported by the National Natural Science Foundation of China (Grant No. 10904008) and the Foundation for Young Scholars of University of Electronic Science and Technology of China (Grant Nos. L08010401JX0806).

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1×10^{18} ions·cm^{-2}. The iron implantation was performed at an energy of 40 keV with nominal doses of 5×10^{17} and 1×10^{18} ions·cm^{-2}. The substrate was kept at room temperature by the circulation of cooling water during ion implantation. The crystalline structure of the material was analysed by x-ray diffraction (XRD) using PHILIPS X'Pert diffractometer with Cu-Kα radiation (=0.154056 nm). The sample stoichiometric compositions were measured by a KRATOS X SAM 800 x-ray photoelectron spectroscopy (XPS). The absorption spectra of the samples were measured on a Shimadzu UV-2500 UV-Visible spectrophotometer. The magnetic properties of the nitrogen implanted samples were analysed using an MPMS XL-7 Magnetic Property Measurement System. The magnetic properties of the iron implanted samples were measured using a vibrating sample magnetometer.

3. Results and discussion

Figure 1 shows the XRD patterns of the pure MgO and nitrogen implanted samples. Only strong (200) diffraction peaks corresponding to rock-salt structure are present for all samples. No other impurity phase is detected by XRD measurement. With the nitrogen dose increasing, the intensity of the (200) diffraction peak is enhanced. However, the peak full width at half maximum (FWHM) is also increased by nitrogen implantation. The FWHMs are 0.42, 1.47 and 1.05 for the pure sample, 1×10^{16} ions/cm^2 and 1×10^{18} ions/cm^2 nitrogen implanted sample, respectively. The FWHM is related to the defects, grain size and residual strain. The intensity of a given reflection (h, k, l) is proportional to the number of h, k, l planes in the diffraction condition. It was reported that MgO films deposited in a nitrogen atmosphere have improved crystallinity compared to films deposited at base-pressure.[9] The (200) peak position shifts from 43.01° for the pure MgO single crystal, to 42.85° for the sample implanted with 1×10^{18} ions/cm^2 nitrogen. The lattice constant α is increased from 4.203 Å (1 Å=0.1 nm) for pure sample, to 4.218 Å for the 1×10^{18} ions/cm^2 nitrogen implanted sample. These increases in lattice constant are consistent with the theoretical results.[7] However, the (200) diffraction peak is weakened by about 6 times by the iron implantation.

The incorporation of nitrogen and iron is confirmed by the XPS measurements. Figure 2 shows the N 1s and Fe 2p XPS signals of 10 nm under the surface. The N 1s signal has a strong peak located at about 399.6 eV. The Fe $2p_{3/2}$ is located at 710.9 eV, which is similar to that of Fe_2O_3. It should be noted that the chemical sate of the implanted ions depends on the depth beneath the surface.[10]

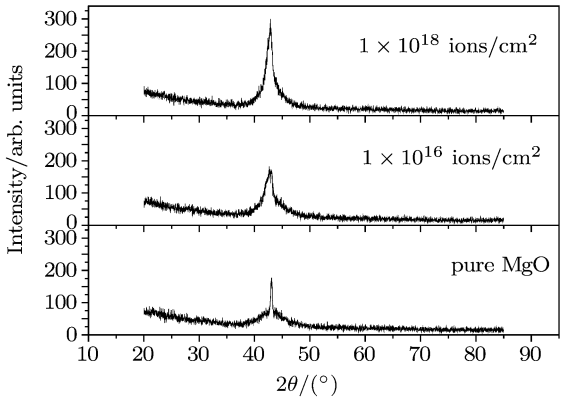


Fig. 1. The XRD patterns of pure MgO and nitrogen implanted samples.

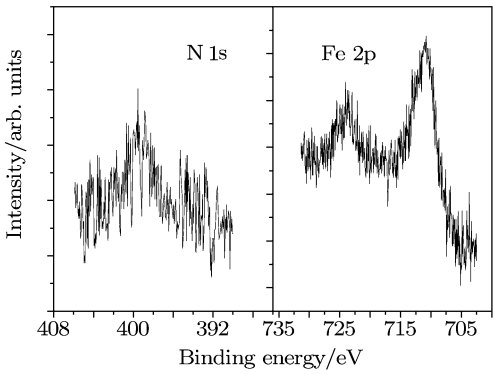


Fig. 2. The N 1s and Fe 2p XPS signals of 10 nm under the surface.

Figure 3 shows the optical absorption spectra for the pure sample, nitrogen and iron implanted samples. Although it was reported by calculation that both substitutional and interstitial nitrogen can generate new energy levels at about 0.5 eV–1.7 eV above the top of the MgO valence band,[11] the optical absorption of the nitrogen implanted sample only demonstrates a small difference compared with that of the pure sample. The pure sample and the nitrogen implanted sample are highly transparent in a region from 1100 nm to 300 nm. However, the optical absorption of the iron implanted samples is greatly enhanced in a region from 210 nm to 1100 nm. As the crystallinity of the iron implanted sample is weakened, the change in absorption may be due to the amorphous phase or to the impurity induced states in the band gap.

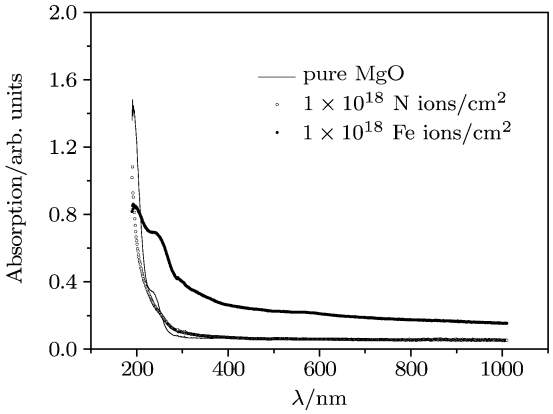


Fig. 3. Optical absorption spectra for the pure, nitrogen and iron implanted samples.

Room temperature hysteresis loops were measured for the pure, nitrogen and iron implanted samples, respectively. Except for the iron and the 1×10^{18} nitrogen ions/cm^2 implanted samples, only diamagnetism is detected for the other samples. Figure 4 shows the room temperature hysteresis loop for the nitrogen and iron implanted samples with a nominal dose of 1×10^{18} ions/cm^2. The diamagnetism from the substrate has been subtracted. The coercivity field and the remanence are about 300 Oe and 38% for the nitrogen implanted sample, respectively. To our knowledge, such large coercivity and remanence are scarcely observed in diluted magnetic semiconductors, except for Co doped SnO_2 powders.[12] figure 4 illustrates that the values of coercivity field and remanence are relatively small (about 60 Oe and 11%) for the iron implanted sample. This is similar to cobalt and nickel-doped MgO,[13,14] Mn-doped SnO_2,[15] and Mn-doped ZnO.[16] The big difference in magnetism between nitrogen and transition metal doped MgO indicates that the magnetism of nitrogen implanted sample is not attributed to any possible magnetic transition metal contamination during the implantation. However, the ferromagnetism in the MgO doped with Ni and Co was attributed to defect-mediated ferromagnetic ordering.[13] In the absence of intrinsic defects such as vacancies and interstitials, the Ni-doped MgO could be paramagnetic.[14] We also found that the saturation magnetization of the iron implanted sample is reduced from 2×10^{-4} emu/cm^2 to 1.17×10^{-4} emu/cm^2 with the sample annealing in vacuum at 200 ^{o}C, which is consist with the reported results.[13,14] As defect induced magnetism of MgO is suppressed by nitrogen doping,[9] the magnetism of nitrogen implanted MgO is not possibly related to structure defects. Since all the samples are insulating, the charge carriers cannot cause the magnetic ordering. Various magnetic interactions (such as the double exchange interaction and super-exchange interaction[17,18]) may be present in the nitrogen implanted MgO sample. More work is required to illustrate the mechanism.

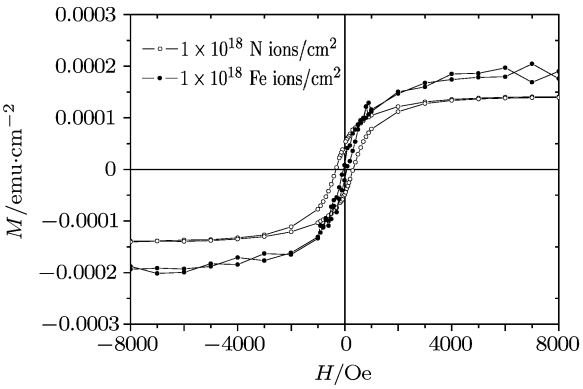


Fig. 4. Room temperature hysteresis loops for the 1×10^{18} ions/cm^2 nitrogen and iron implanted samples.

4. Conclusion

The microstructure, optical and the magnetic property of nitrogen and iron implanted MgO single crystal are investigated. The optical absorption has a small dependence on the nitrogen impurity concentration. MgO changes from diamagnetic to ferromagnetic at room temperature when the nitrogen dose increases to 1×10^{18} ions·cm^{-2}. The coercivity field is about 300 Oe. However, the coercivity field of iron implantation with the same dose is only 60 Oe. Furthermore, compared with the nitrogen implantation, the iron implantation has a different effect on the crystal structure and optical absorption.

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