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Effect of 80 keV Ar^+ implantation on the properties of pulse laser deposited magnetite (Fe_3O_4) thin films

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Abstract. Highly oriented thin films of Fe_3O_4 were deposited on (100) $LaAlO_3$ substrates by pulsed laser ablation. The structural quality of the films was confirmed by X-ray diffraction (XRD). The films showed a Verwey transition near 120 K. The films were subjected to 80 keV Ar^+ implantation at different ion doses up to a maximum of 6×10^{14} ions/cm^2. Ion beam induced modifications in the films were investigated using XRD and resistance vs temperature measurements. Implantation decreases the change in resistance at 120 K and this effect saturates beyond 3×10^{14} ions/cm^2. The Verwey transition temperature, T_V, shifts towards lower temperatures with increase in ion dose.

Keywords. Implantation; magnetite; thin films; pulsed laser ablation; Verwey transition.

1. Introduction

Magnetite (Fe_3O_4) is one of the most intensively studied oxides over the past few decades because of its unique electrical and magnetic properties (Verwey 1939; Verwey and Haayman 1941; Verwey *et al* 1947; Kazlowaski *et al* 1993). At room temperature, it crystallizes in the inverse spinel structure with Fe^{3+} at tetrahedral or A sites while octahedral or B sites are occupied by a mixture of Fe^{2+} and Fe^{3+}. At high temperatures, the cation distribution becomes random. Magnetite is a ferrimagnet with a Curie temperature of 858 K (Keffer 1966). The temperature dependent electrical resistivity of Fe_3O_4 shows interesting features related to structural and magnetic phase transitions. It has already been reported (Hamilton 1958) that even at temperatures above 300 K, although the structure remains cubic, there is a magnetic phase transition from the ferrimagnetic to the paramagnetic state at a Curie temperature, T_C. In this temperature range, the transport of electrons can be described by the hopping model and a sharp discontinuity occurs at T_C, mainly due to the spin disordering of the Fe^{2+} and Fe^{3+} ions. At temperatures below 300 K, initially the resistivity increases very slowly as the temperature decreases. However, at around 120 K, the electrical resistivity of Fe_3O_4 increases by almost two orders of magnitude (Verwey 1939; Verwey and Haayman 1941; Verwey *et al* 1947). This change in the resistivity is called the Verwey transition and the corresponding temperature at which this transition takes place is known as the Verwey transition temperature (T_V).

The sharp change in the electrical resistivity of the bulk material by nearly two orders of magnitude at around 120 K is due to a first order thermodynamic transition (Verwey and Haayman 1941; Verwey *et al* 1947). Due to the mixed valence, hopping of electrons at octahedral site takes place easily from Fe^{2+} to Fe^{3+}, which leads to a high conductivity at room temperature (Kazlowaski *et al* 1993). The simplistic picture is that Fe^{2+} and Fe^{3+} ions occupying the octahedral (B) sites get ordered below T_V and result in an order–disorder transformation, in which the distribution of Fe^{2+} and Fe^{3+} ions changes from a dynamic disorder to an ordered state on the octahedral sites. Anderson (1956) interpreted the Verwey transition as a loss of the long-range order of the 'extra' electrons on the octahedral site at temperatures above T_V while the short-range order is maintained across the transition. Cullen and Callen (1971, 1973) proposed a simple model in which the 'extra' electrons on the B sublattice move in a nondegenerate spinless band. Such a model has two parameters, viz. the tight-binding integral related to the bandwidth of the 'extra' electrons and the nearest neighbour coulomb repulsion. Isotope substitution experiments (Terukov *et al* 1979) suggest that electron–phonon coupling leading possibly to polaron formation, might play some role in the Verwey transition. According to Yamada's (1980) molecular polaron picture, the Verwey transition is viewed as a cooperative ordering of the molecular polarons presumed to interact via the strain fields that they generate. According to Mott (1990), at low temperatures (below 120 K) Fe_3O_4 is a Wigner glass, and with increase in temperature, the lattice 'melts' resulting in disappearance of the long-range order.

The Verwey transition temperature was found to be maximum for pure stoichiometric Fe_3O_4, which decreases

from 120 K to about 81 K with increasing departure from stoichiometric composition (Kakol 1990). A small orthorhombic distortion has been detected by X-ray measurements (Abrahams and Calhoun 1953, 1955) and more direct verification of the ordered state below T_V has been provided by neutron diffraction (Hamilton 1958). The ordering of Fe^{2+} and Fe^{3+} on the B sublattice affects the magnetic anisotropy of the system and this oxide is much harder to magnetize and saturate below T_V (Weiss and Forrer 1929; Palmer 1963). The Verwey transition in magnetite also represents a well-defined phase transformation in a thermodynamical sense explained by Kakol (1990) on the basis of specific heat measurements.

In the present work, the effect of ion implantation on the structural and transport properties of Fe_3O_4 thin films has been examined. The Verwey transition in this material system was studied as a function of ion dose. Since implantation can lead to a controlled introduction of defects and dopants in a material system, studies of implantation have a potential to generate new information on this material system.

2. Experimental

The a-Fe_2O_3 target used for the deposition of Fe_3O_4 thin films was prepared by the standard ceramic technique and was sintered at 950ºC in air at atmospheric pressure for more than 20 h. Growth of epitaxial Fe_3O_4 films on (100) $SrTiO_3$, (0001) a-Al_2O_3, (001) MgO and (100) $LaAlO_3$ substrates has been reported (Fujii *et al* 1994; Kennedy 1995; Ogale *et al* 1998). In the present study, Fe_3O_4 films (2500 Å thick) were deposited on (100) $LaAlO_3$ substrates by pulsed laser deposition (PLD), using a KrF excimer laser (Lambda Physik LPX2000, l = 248 nm, t_p = 20 ns). The substrates were ultrasonically cleaned in trichloroethelene prior to deposition. During PLD, the laser energy density was 2 J/cm^2 at the target and the substrate temperature was 610°C. The distance between the target and the substrate was 4 cm. The oxygen partial pressure during deposition was maintained at 1×10^{-4} mbar and it was raised to 1 bar during cooling of the substrate. The high crystalline quality of the as-deposited films was confirmed by X-ray diffraction (XRD) method (Philips PW1840). In the present study Cu target was used and CuK_a radiation was selected from X-ray source with 1·542 Å wavelength. The thickness of the films was determined by using Hobsen-Taylor talystep apparatus. The electrical resistivity measurements were carried out using the four-probe (co-linear) method. The current was supplied from a programmable constant current source (Keithley model 220) through the outer two probes and the voltage developed was measured by nanovoltmeter (Keithley model 181) across the two inner probes. The low temperature (< 300 K) of the sample was measured by silicon diode connected to a temperature controller (model DRC91C Lakeshore Cryotronics Inc.). The Fe_3O_4 film was then implanted at room temperature with Ar^+ ions of energy 80 keV at different fluences up to a maximum fluence of 6×10^{14} ions/cm^2. The projected range of 80 keV Ar^+ in Fe_3O_4 was 520 Å, which was calculated by using the Transport of Ion in Material (TRIM 94) code (Ziegler *et al* 1985). The implantations were carried out with 300 kV ion implanter (Ogale 1990). The film was kept at an angle of 7° with the plane normal to the incident Ar^+ ion beam to reduce the channelling of the incoming ions. To avoid bombardment induced heating, the fluence rate was maintained at 1 μA/cm^2. A liquid nitrogen cooled jacket was used around the target to avoid unintentional carbon contamination during implantation. The implanted film was characterized by XRD and resistance vs temperature measurement after each ion dose of implantation. It may be noted that the same film was used for various doses of implantation.

3. Results and discussion

Figure 1a shows the XRD pattern for the virgin Fe_3O_4 film deposited by PLD on (100) $LaAlO_3$ substrate. The (220) and (440) peaks of Fe_3O_4 are very sharp, indicating highly oriented nature of the as-deposited film. Figure 2 shows the $\ln[R_T/R_{77\,K}]$ vs $1000/T$ curve for the virgin film. It shows an increase in the value of resistance by two orders of magnitude near 120 K indicating the Verwey transition. The jump in the resistance is strongly dependent on the deposition conditions such as substrate temperature and oxygen partial pressure during the deposition. The activation energy, E_{act}, for hopping of electrons is calculated from $\ln[R]$ vs $1/T$ curve in the semiconducting region between 140 K and 300 K using the Arrhenius equation. It is found to be 71 meV for the virgin sample, which matches well with the data, reported earlier for Fe_3O_4 thin films (Aragon 1992; Kazlowaski *et al* 1993).

Figures 1b–d show XRD patterns for the 80 keV Ar^+ implanted samples at various dose values. The (220) and (440) peak intensities are found to slowly reduce upon Ar^+ implantation. No appreciable change in the peak broadening and/or relative intensities of the (220) and (440) peaks is observed. The (220) and (440) peaks in the XRD pattern do not disappear even at the highest dose value of 6×10^{14} ions/cm^2. However, the positions of (220) and (440) peaks are seen to shift to lower $2q$ values as the dose increases, implying a decrease in the c-axis lattice constant.

Figure 2 shows $\ln[R_T/R_{77\,K}]$ vs $1000/T$ curves for the virgin film and the same film implanted with 80 keV Ar^+ at different dose values. The resistance is normalized to that at 77 K. The film both before and after implantation at various doses shows the Verwey transition feature near

120 K. The change in the electrical resistance due to order–disorder transition is more prominent in as-deposited Fe_3O_4 film. The behaviour shows interesting features in the vicinity of the transition temperature T_V. The change in the resistance at 120 K is less for all the doses as compared with the as-deposited film (figure 2). It is seen that the transition temperature shifts towards the lower temperature side as the dose increases. The Verwey transition temperature in magnetite is sensitive to the Fe/O ratio (Aragon *et al* 1886), the number of Fe^{2+} ions available for the conduction, and the addition of divalent impurities (Kakol 1990) like Cu^{2+}, Zn^{2+}. In the present study, the transition temperature shifts towards lower temperatures, which indicate change in the oxygen stoichiometry and the Fe/O ratio due to implantation (Kuipers and Brabers 1976; Gillot and Jemmali 1983). Verwey and Haayman (1941) had reported that an increase in the oxygen content of the Fe_3O_4 phase shifts the transition from 120 K to 100 K and that the jump in the resistance at the transition decreases.

The activation energy (between 300 and 140 K) for the electron conduction of the as-deposited film is 71 meV. As the dose value increases, the activation energy reduces which is expected for such a system as shown in figure 3. In the same figure, the rate of change of resistance with temperature (dR/dT), in the vicinity of Verwey transition versus ion dose is also plotted. For the as-deposited film dR/dT is 40 Ω/K. As the dose is increased, the rate of increase of resistance in the vicinity of T_V becomes slower. Beyond the dose of 1×10^{14} ion/cm^2, this effect is found to saturate and thereafter, further increase in the Ar ion dose does not affect the activation energy and dR/dT.

The XRD and R vs T results can be interpreted as follows. As-deposited Fe_3O_4 film shows a well-defined Verwey transition. At temperatures below T_V, Fe^{2+} and Fe^{3+} ions on the octahedral sites become ordered along mutually perpendicular directions (Verwey 1939; Verwey and Haayman 1941; Verwey *et al* 1947), causing localization of electrons, and hence, large change in the resistance at T_V. Ion implantation induces local disorder in the film as seen from the decrease in the XRD peak intensities. The remaining regions are then strained, as reflected by c-axis contraction, which in turn give rise to orbital overlapping (Ramasesha *et al* 1994). As the dose is increased, because of the increase in orbital overlap, Fe_3O_4 becomes more metallic, as seen from the decrease in the resistance.

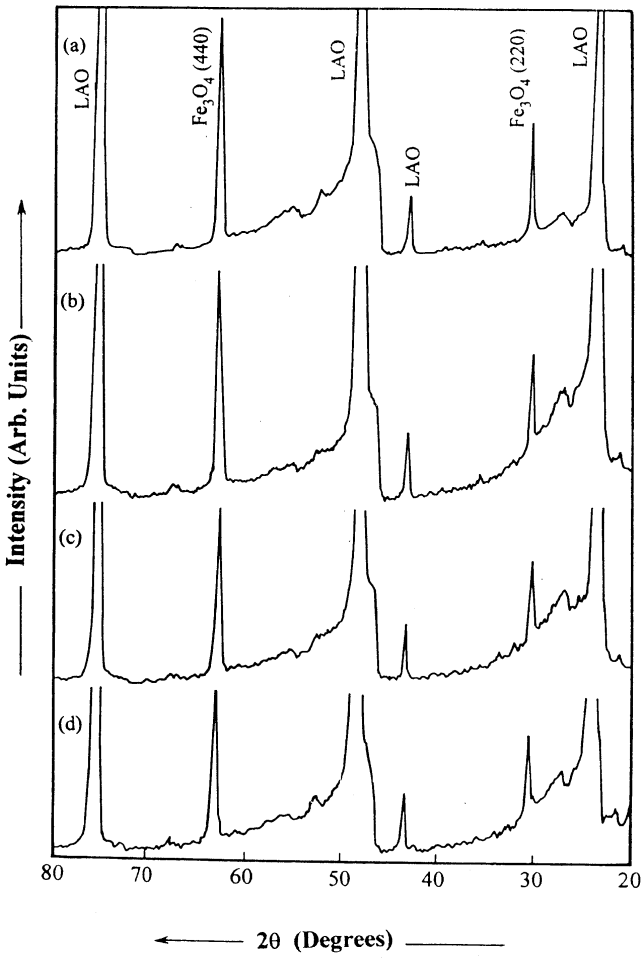

Figure 1. XRD patterns for (a) virgin Fe_3O_4 film deposited on (100) $LaAlO_3$, film implanted with 80 keV Ar^+ at (b) 1×10^{13} ions/cm^2, (c) 1×10^{14} ions/cm^2, and (d) 6×10^{14} ions/cm^2.

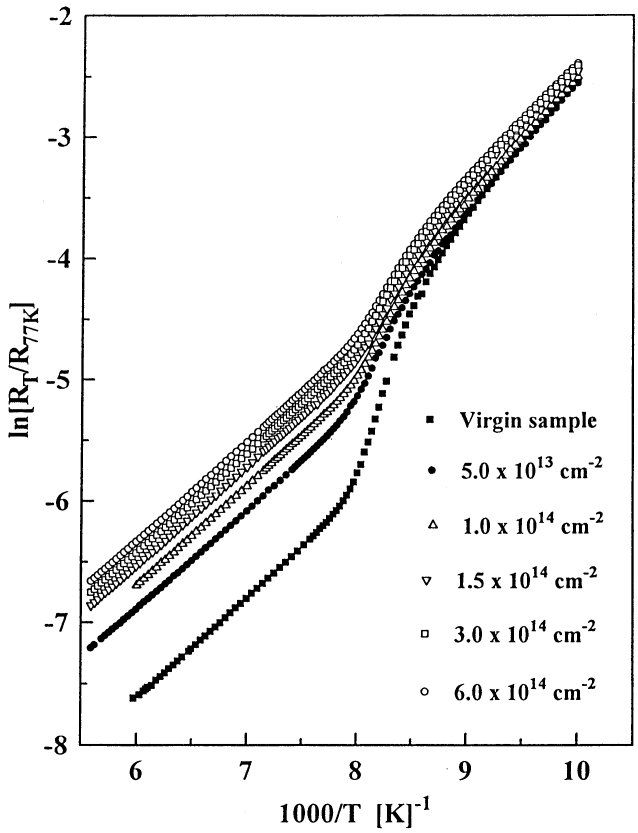

Figure 2. $R_T/R_{77\,K}$ vs $1000/T$ curves for the virgin as well as implanted samples.

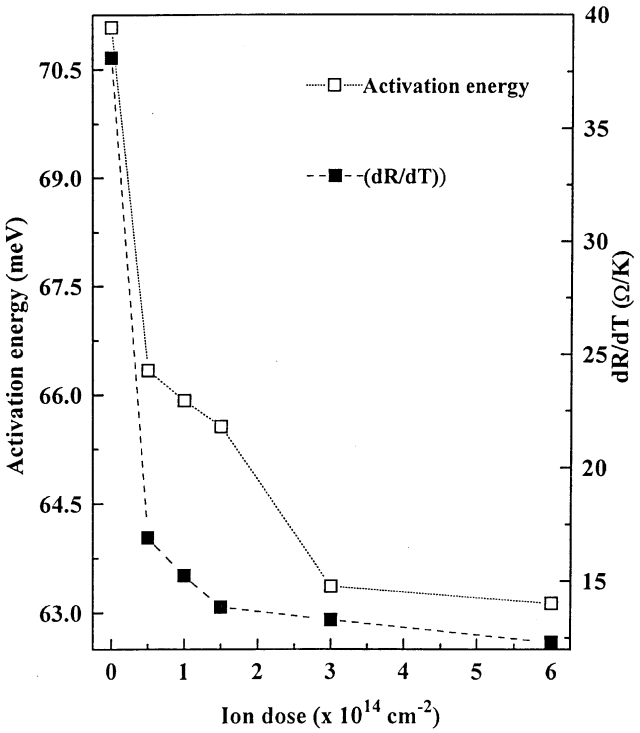

Figure 3. Activation energy for the electron conduction and d*R*/d*T* vs temperature.

Clearly, there is greater delocalization of electrons and a suppression of cation ordering with increasing ion dose. With increasing dose, the Verwey transition behaviour is significantly suppressed, and for the film implanted at a dose of 6×10^{14} ions/cm^2 very small change in the resistance at 120 K as compared to as-deposited film is observed. Defects formed due to implantation also play an important role in the conduction mechanism. Different types of defects such as Schottky and Frenkel defects are generated in the film when it is bombarded with 80 keV Ar^+ (Williams 1986). Due to these defects there may be a change in the distance between Fe^{2+} and Fe^{3+}. This change can lead to increased conductivity as observed with suppression of Verwey transition.

4. Conclusion

Highly oriented Fe_3O_4 films were successfully deposited on (100) $LaAlO_3$ substrates, using the PLD technique. The as-deposited film shows a significant change in resistance value around 120 K and the activation energy (between 300 and 140 K) for the electrical conduction is 71 meV. Ar^+ implantation decreases the change in the resistance at 120 K and this effect gets saturated at doses beyond 3×10^{14} ions/cm^2. Below the Verwey transition temperature T_V, long-range order is favoured in a single crystal film of Fe_3O_4. In implanted samples, the Verwey transition temperature, T_V, shifts towards lower temperatures as the ion dose is increased.

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