

Study of surface morphology and grain size of irradiated MgO thin films

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ABSTRACT

Present work reports 200 MeV Ag¹⁵⁺ irradiation induced effects on the surface morphology, grain size and local electronic structure in MgO thin films deposited by e-beam evaporation under ultra High vacuum. The grain size was found to decrease from 37 nm (pristine film) to 23 nm for the sample irradiated with fluence of 1×10^{12} ions/cm² and thereafter it increases upto fluence of 5×10^{12} ions/cm². Similar changes with ion fluence were also observed for surface roughness. Shifting and disappearance of peaks in X-ray absorption spectra with irradiation shows the electronic structure modification after irradiation. The detailed analysis of observed results has been done on the basis of existing theories. Copyright © 2012 VBRI Press.

Keywords: MgO; atomic force microscopy; X-ray absorption spectroscopy.



Jitendra Pal Singh did Ph. D. from Govind Ballabh Pant University of Agriculture and Technology, Pantnagar, Uttarakhand in 2010. He worked as a Research Associate at Inter-University Accelerator Centre, New Delhi during 2010-2011. Presently, he is working as a post-doc researcher at Taiwan SPIN Research Centre, National Chung Cheng University, Taiwan. His research interests are irradiation studies in nanoferrites, thin films and magnetic multilayer.



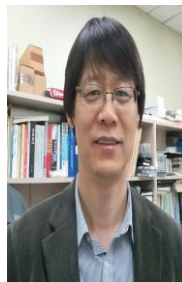
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Introduction

In current scenario tailoring properties of materials by swift heavy ions (SHIs) is an important topic of research for scientific community. It not only produces the materials with desired properties but also helps in understanding the fundamentals of ion-solid interaction by choosing different kinds of materials such as polymers, granular structures, functional oxides, single crystals etc [1-7]. Generally, SHIs are known as the fast heavy ions with energies \sim MeV/amu. These ions while passing through the materials lose energy in the medium which in per unit length is called as stopping power (S) and arises by two main contributions: (i) electronic excitations, and (ii) nuclear excitations. The energy loss per unit length in the materials by these two processes is called as electronic stopping (S_e) and nuclear stopping (S_n) respectively. The dominant S_e value in the system directly enables to the role of electronic excitation in determination of the irradiation induced modified properties by producing different types of defects in the system. In most of the irradiation experiment SHI induced modifications have been studied by keeping S_e/S_n ratio of 10^3 [8-9]. For better understanding of these excitations in materials MgO was selected. This system has rocksalt structure and electrically insulating and its optical band-gap is 7.6 eV. MgO has become focus for intense research activities for understanding of d^0 ferromagnetism and its use in magnetic tunnel junctions [10-13]. Theoretical investigations on this system indicate that presence of defects greater than a threshold value is responsible for the magnetic behaviour that can be tuned by controlling film thickness, fabrication process and size of nanoparticles [10, 11]. So far, many methods are reported for depositing oxide thin film like rf sputtering [12, 13], pulsed laser deposition [14] and e-beam evaporation [15]. Out of these methods e-beam evaporation is low cost and effective for depositing oxygen efficient thin films of MgO [15].

Hence, for present work, we have studied the irradiation induced effects in MgO thin film deposited on quartz substrate deposited by using e-beam evaporation. Atomic force microscopy (AFM) has been distinguished as a powerful tool to study the surface morphology of the irradiated systems. Besides this X-ray absorption spectroscopy (XAS) has been used to investigate the local electronic structure of these materials.

Experimental

Deposition of films

MgO thin films of thickness 50 nm were deposited on quartz substrate by using e-beam evaporation under the base pressure better than 5×10^{-8} Torr. MgO powder (Alfa Aesar, 99.99%), pressed into the form of pellets of diameter 6 mm, and was used for evaporation. Thickness of the films was monitored using quartz crystal monitor deposition rate 1.0 \AA/s and substrate temperature was maintained at room temperature.

Ion beam irradiation and parameters

MgO thin films were irradiated by 200 MeV Ag^{15+} ion beam using Pelletron Accelerator, Inter University Accelerator Centre (IUAC), New Delhi in high vacuum

($\sim 10^{-6}$ Torr) at the fluence of 1×10^{11} , 5×10^{11} , 1×10^{12} , 3×10^{12} and 5×10^{12} ions/cm². The values of electronic stopping, nuclear stopping and projected range of 200 MeV Ag ions for MgO are 9.33, 0.0229 keV/nm and 32 μm respectively [16]. In the present work S_e/S_n ratio is $\sim 4 \times 10^2$, hence the role of nuclear stopping is neglected. The projected range of the ions is more than the thickness of film, hence the possibility of implantation of ions in the film is completely ruled out.

Characterization of thin films

X-ray diffraction (XRD) pattern of the pristine and irradiated samples has been recorded by Bruker D8 Advacne X-ray diffractometer. AFM images were taken in tapping mode at the room temperature using NanoScope IIIa SPM at IUAC, New Delhi. Further, electronic structure of irradiated system has also been investigated by Near-edge X-ray absorption fine structure (NEXAFS). NEXAFS spectra were collected at the high energy spherical grating monochromatic (HSGM) beamline in the National Synchrotron Radiation Research Centre in Taiwan. All measurements were processed in an ultra high vacuum (UHV) chamber. As collecting O K-edge XAS spectra, the spectrum of a CuO single crystal were measured simultaneously in a separate chamber, which enabled us to achieve energy calibration better than 0.01 eV accuracy. The UV-Vis spectra of the pristine and irradiated films were recorded on Varian UV-Vis spectrometer.

Results and discussion

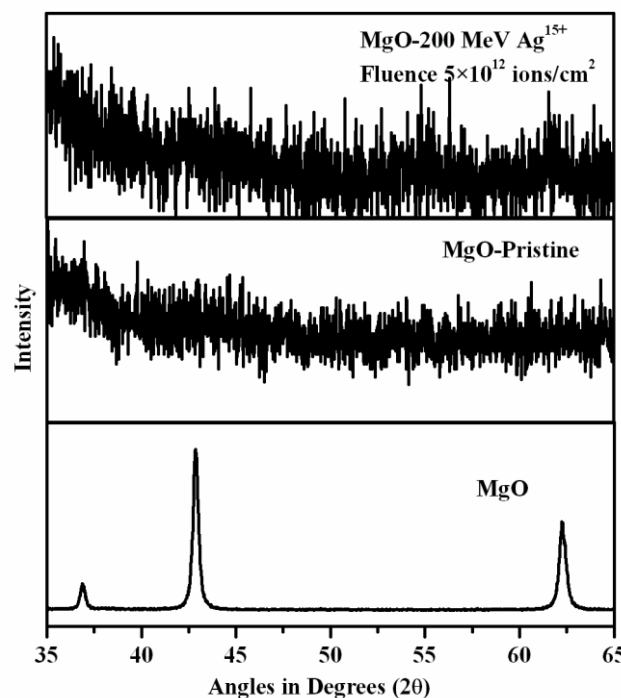


Fig. 1. X-ray diffraction pattern of MgO, MgO-Pristine and irradiated with 200 MeV Ag^{15+} at fluence of 5×10^{12} ions/cm².

Fig. 1 shows XRD pattern of MgO-target, pristine film and film irradiated with 200 MeV Ag^{15+} ion beam at fluences 5×10^{12} ions/cm². It is clear from the **fig. 1** that MgO target exhibit pure phase of rocksalt structure, however as-deposited (pristine) MgO film exhibit

amorphization nature of these films. Even, after irradiation there is not improvement in the structural properties as can be clearly observed from the XRD pattern of irradiated at the fluence of 5×10^{12} ions/cm².

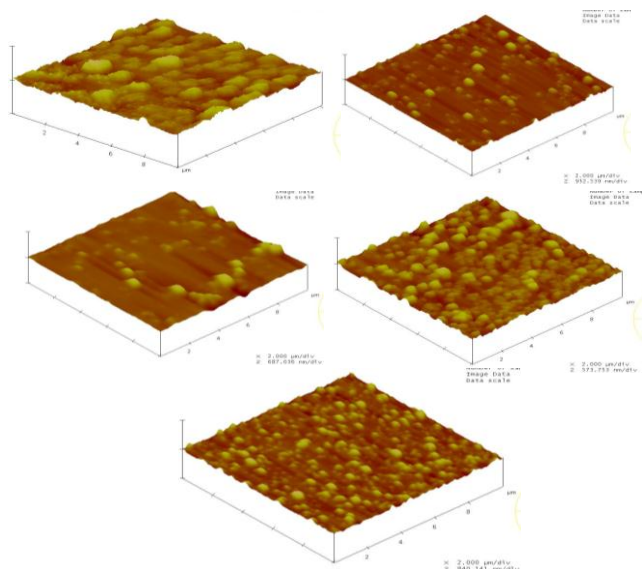


Fig. 2. AFM images of MgO-Pristine and irradiated with 200 MeV Ag¹⁵⁺ at different fluence.

Fig. 2 exhibits the surface topology of the MgO thin film irradiated with 200 MeV Ag¹⁵⁺ at different fluences. The detailed investigation on the changes in topological nature of irradiated MgO thin film has been carried out by estimating the grain size, size distribution and surface roughness.

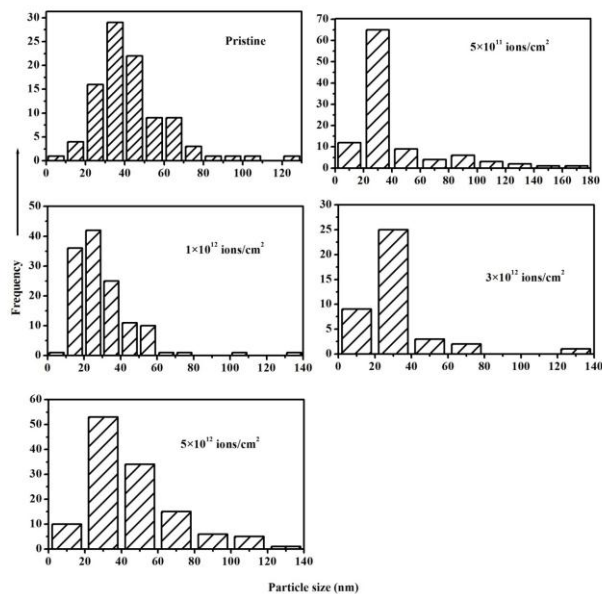


Fig. 3. Grain size distribution of MgO-Pristine and irradiated with 200 MeV Ag¹⁵⁺ at different fluence.

A visual inspection of **Fig. 3** shows the change in size distribution with increasing ion fluence and systematic change could be observed. Pristine film shows wide distribution of the particle size with the average size of 35-40 nm, as fluence is increased, the size distribution narrows

down with the maximum particles of size centered around ~35 nm, when irradiated at fluences 1×10^{12} ions/cm². On further increasing fluence upto 5×10^{12} ions/cm², average particle size do not changes much but decreases slightly ~ 30 nm (**Fig. 3**). From the graphs we can see that that average particle size is reducing and the particles are more ordered in terms of their distribution at increasing ion fluences. The pristine sample has clusters of bigger particles, upon irradiation these clusters breaks into smaller particles as can be observed in AFM micrographs in **Fig. 2**. After irradiation, the particles number density reduces upto fluence of 1×10^{12} ions/cm² and increases again with increasing fluence upto 5×10^{12} ions/cm². Similarly, grain size of film also decreases with ion fluence upto 1×10^{12} ions/cm² and increases onwards with increasing ion fluence. Decrease in grain size with fluence of irradiation results due to fragmentation caused by strain develop during irradiation [17]. Similar effect has been observed in LiF thin films and explained on the basis of both the thermal spike and coulomb explosion model [18]. It has been reported that for LiF, grain size decreases with fluence and after a particular value of fluence there is no further reduction in grain size. It has been explained by claiming that there may be critical size of the grain for which the surface energy is too high to be fragmentation [18].

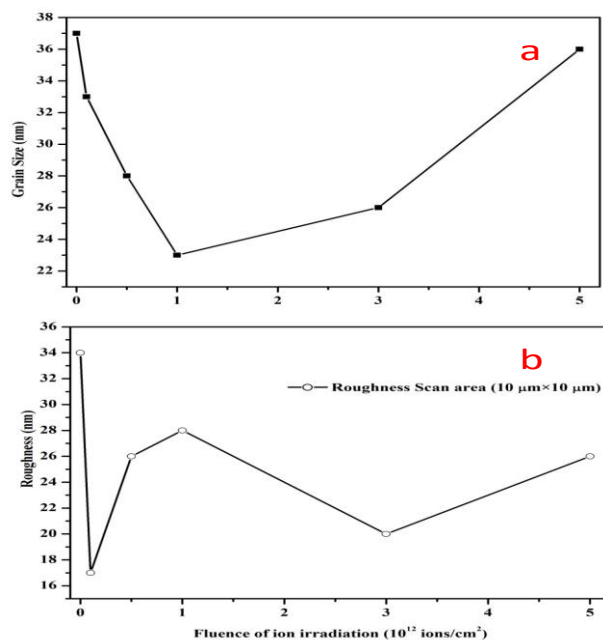


Fig. 4. (a) Grain Size and (b) surface roughness of MgO thin film irradiated with 200 MeV Ag¹⁵⁺ beam at different fluence.

However, our results shows increase in grain size after particular value of fluence (**Fig. 4a**). D. Kaoumi et al. [19] proposed a model for grain growth under the effects of ion irradiation and shown that growth occurs after a threshold value of increase in local temperature. In present case, these effects occur for MgO after the fluence of 1×10^{12} ions/cm². The estimated surface roughness for scan area of $10 \mu\text{m} \times 10 \mu\text{m}$ is shown in **Fig. 4b**. No regular trend of the surface roughness with fluence of irradiation was observed in the present work (**Fig. 4b**). Change in surface roughness

during ion irradiation is due to competition between multiple roughening and smoothing processes. The roughness of the film do any exhibit any regular variation with fluence. Random arrival of the ion on the surface results in stochastic roughening process while smoothing mechanisms on the surface include surface diffusion, viscous flow, sputter redeposition, and sputter removal affected by shadowing processes [20, 21].

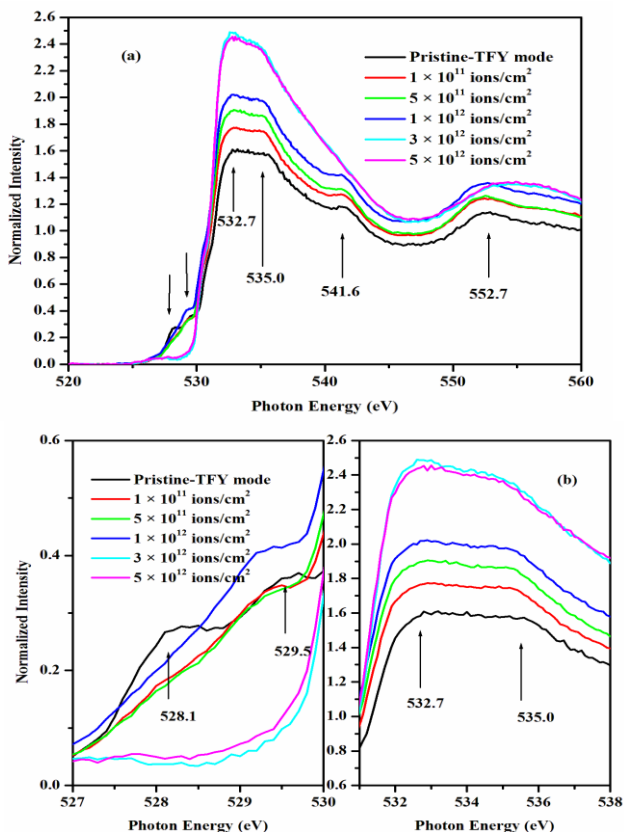


Fig. 5. X-ray absorption spectra (TFY mode) of MgO thin film irradiated with 200 MeV Ag^{15+} beam at different fluence.

It has been discussed that excess amount of energy transferred to the system confined within grain volume and give rise to excitation of electronic states [22]. This effect has been investigated by X-ray absorption spectroscopy (XAS). **Fig. 5** and **6** show the XAS spectra at O-K-edge of the pristine and irradiated films in total electron yield (TEY) and total fluorescence yield (TFY) mode. To understand the irradiation induced effects on the electronic structure, we have separately discussed the XAS spectra of both these modes. O-K edge spectrum in TFY mode for the pristine sample exhibits major spectral peaks at 532.7, 535.0, 541.8 and 552.7 eV, which are characteristics of MgO [23]. This spectrum also consists of pre-edge region with two peaks: ~ 528.1 and 529.5 eV (**Fig. 5**). Presence of this region is due to the excitation to the localized bound state and consistent with the previous reports of XAS study of MgO [23]. Pre-edge region of the spectrum is modified significantly by the fluence of irradiation. The peak around 528.1 eV starts to disappear for the fluence of 1×10^{11} ions/cm² and completely disappear at the fluence of 3×10^{12} ions/cm². Apart from this the peak around 529.5 shifts towards lower value with fluence and disappear at the

fluence of 3×10^{12} ions/cm² (**Fig. 5a**). Similar to this peak around 541.8 also disappears at same fluence (**Fig. 5**). The intensity of the peaks around 532.7 and 535.0 decreases with fluence and exhibit sudden enhancement at the fluence of 3×10^{12} ions/cm² and onwards (**Fig. 5b**). Apart from this spectral features in TEY mode exhibit dominant changes after the fluence of 1×10^{12} ions/cm². The dominant spectral features in the pristine film for this mode are 526.5, 528.3, 529.5, 535.3 and 539.9 eV (**Fig. 6**).

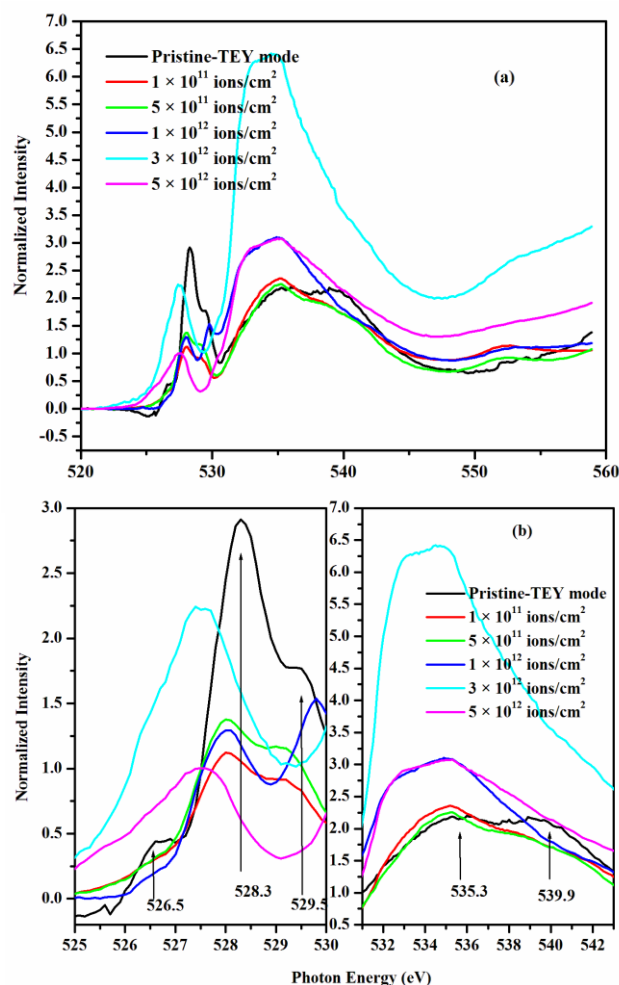


Fig. 6. X-ray absorption spectra (TEY mode) of MgO thin film irradiated with 200 MeV Ag^{15+} beam at different fluence.

In this film all the spectral features are clearly distinguishable. With irradiation peaks corresponding to these features in both the modes exhibit shifting towards lower values. Increase in intensity of spectral features also appears after the irradiation. The dominant changes in the spectral features after irradiation in TEY mode as compared to TFY mode are due to the surface sensitive nature of TEY mode. The changes in various spectral features with irradiation are attributed to the modifications induced by electronic excitation in the system, which increases empty states in the system. Modifications in electronic structure of the irradiated system may also lead to the change in optical absorbance of the system. Hence the optical absorption spectra of the pristine and irradiated films were recorded and shown in **Fig. 7**. Slight increase in optical absorption in visible region in the irradiated film

may be due to the irradiation induced defect creation like anti-site oxygen and oxygen vacancies [25]. In the spectra of irradiated films a peak appears ~ 250 nm. This peak generally observed in the films irradiated with quartz substrate [25] but this peak was also observed in irradiated MgO single crystal [26]. This peak has been assigned due to F-type centers (oxygen vacancies with trapped electrons), which were also created during ion irradiation. Hence by analogy produced oxygen vacancies after irradiation results in change in the XAS spectra of the irradiated specimen.

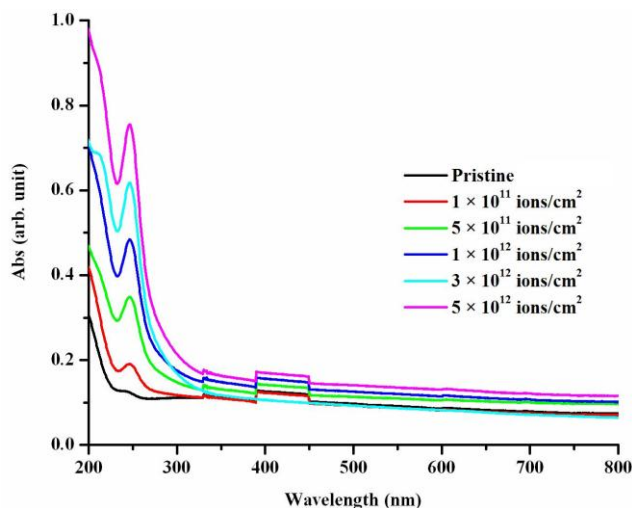


Fig. 7. Optical absorption spectra of MgO thin film irradiated with 200 MeV Ag^{15+} beam at different fluence.

Conclusion

Present study shows that amorphized nature of as deposited MgO could not be improved by irradiation with 200 MeV Ag^{15+} . The decrease in grain size of the film upto the fluence of 1×10^{12} ions/cm² has been attributed to the fragmentation caused by strain develop during irradiation. The increase in grain size after this fluence shows increase of local temperature above a threshold value that induces grain growth. Change in roughness of the film after irradiation may be attributed to the effect of surface modification after irradiation. It may be contemplated that electronic excitation produced in the system during irradiation results in the change of local electronic structure of the system which has been clearly observed in our XAS study.

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