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Tailoring of optical and gas sensitivity behaviors of WO_3 films by low energy Ar^+ ion implantation

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ABSTRACT

In this paper we report the structural, optical and gas sensitivity behaviors of WO_3 films implanted by 100 keV Ar^+ ions. The films have been deposited on the unheated corning glass and n-type Si (100) substrates by thermal evaporation technique. The structural and vibrational properties of the pristine and implanted films have been thoroughly studied using X-ray diffraction patterns and Raman micrographs respectively. Optical transmittance and reflectance spectra of the films in the wavelength range 300 to 1000 nm have been measured. An increase in optical band gap from 2.90 to 3.49 eV has been observed with the increase in fluence from 3×10^{15} to 1×10^{17} cm^{-2}. It is also observed that implantation has caused enhancement in photoluminescence yield of the films. All films, especially the implanted films have shown good gas sensing behavior in methane environment. The film with a critical fluence of value 1×10^{16} cm^{-2} shows better optical as well as gas sensing behaviors and hence can have good device applications.

1. Introduction

Tungsten trioxide (WO_3) is one of the transition-metal oxides and has a wide indirect band gap. It almost always exhibits strong n-type conductivity and is optically transparent towards UV and visible regions [1,2]. Due to electrochromic behavior of this compound, WO_3 films are presently used in sunglasses, automotive rear-view mirrors and sun roofs etc. [3,4]. Another potential application of WO_3 thin films is in aerospace industry for infrared emissivity modulation and temperature control in spacecraft [5]. Furthermore, it has been demonstrated that WO_3 thin films exhibit chemical sensing properties [6,7] and can have applications in environmental pollution monitoring, particularly in monitoring hazardous gases such as H_2S, NO and NO_2 etc. Recently Tesfamichael et al. have reported that Fe doped WO_3 films show reasonably good gas sensing behavior in acetaldehyde (CH_3CHO) environment [8].

Out of several techniques helpful for monitoring the basic behavior of the materials, ion implantation is very useful for impurity doping and defect production in materials to make them suitable for device fabrication. It also helps to alter the structural, optical, magnetic and vibrational properties of the materials [9,10]. A literature survey reveals that the majority of studies on implanted WO_3 films have focused on the modification in their electrical and optical properties because of ion implantation [11–13]. For example, Miyakawa et al. [12] have observed that after implantations of 90 keV He^+ and 360 keV Ar^+ ions, electrical conductivity of WO_3 films increases significantly. They have argued that such rise in conductivity can be attributed to the formation of charged oxygen vacancies because of nuclear collisions that occur during implantation. From Hall measurement the same group has also reported that the conductivity of the WO_3 film increases by H^+ and He^+ implantations because of increase in carrier mobility [14]. Sivakumar et al. [15] have observed a rise in conductivity and reduction in band gap value of WO_3 films using 2 MeV N^+ ion implantation. In case of 100 keV Er^+ implanted WO_3 films; Mohamed et al. [16] have observed a strong increase in conductivity due to ion implantation and a moderate decrease in transmittance in the visible and near infrared regions with almost unchanged band gap. Wagner et al. have observed enhancement in the refractive index of WO_3 films because of N^+ ion implantation [17]. Inouye et al. [18] have studied the relation between hydrogen retention and optical properties of amorphous films of WO_3 using 10 keV H_2^+ ion implantation.

In this paper, we report the effect of 100 keV Ar^+ ion implantation in WO_3 thin films with different fluences. We have made a thorough study on implantation induced modification of structural, morphological, optical and gas sensing properties of the films. We started this work with some motivation that since implantation of Ar^+ ions is expected to cause increase in oxygen vacancies in the films without formation of any new compound; such type of implantation may bring a favorable change in different characteristic properties of the films. In case of SiO_2 film, Holgado et al. [19] have observed that

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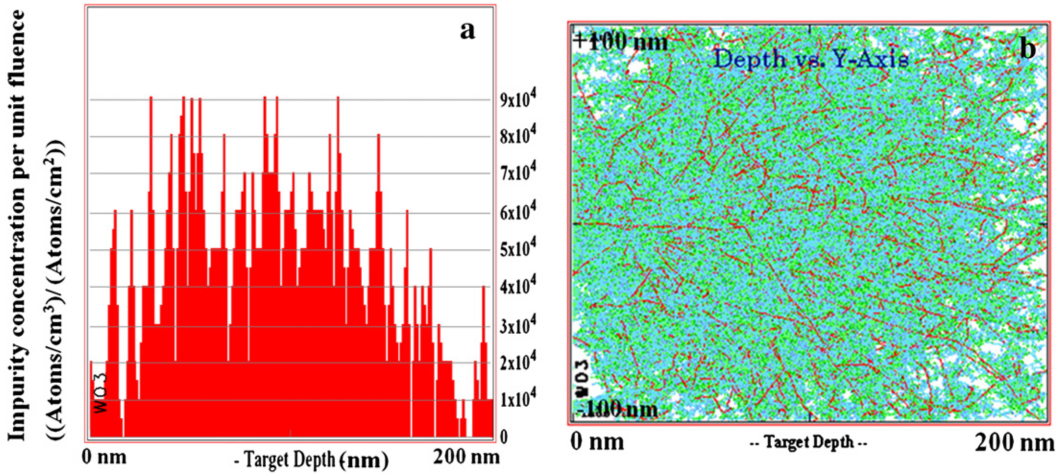

Fig. 1. (a) Implantation profile of Ar^+ ions as a function of target depth versus Y-axis. (b) Monte Carlo simulation of Ar^+ ion implantation in WO_3 film.

bombardment by He^+ and Ar^+ ions does not cause formation of any new compound as these are inert gas ions; only the sample loses oxygen. But in case of N^+ ion bombarded SiO_2 film a new silicon oxynitride compound is formed [19]. Some previous reports on ZnO films implanted by He^+ and Ag^+ ions reveal that implantation can be considered as a possible mechanism for enhancing gas sensitivity [20,21]. Liao and co-workers [20] have also found that the gas sensitivity of the ZnO nanowires can be modulated and enhanced by He^+ ion implantation. However, such studies are less in number and more extensive work in this direction is still required.

2. Experimental details

WO_3 films were deposited on the unheated corning glass and n-type Si (100) substrates by thermal evaporation of high-purity WO_3 powder (99.99%), taken in water cooled sapphire boat. The substrates were cleaned with trichloroethylene, isopropanol, acetone and deionized water before introducing it into the evaporator. The distance between the source and substrates was ~20 cm and the base pressure in the evaporator was 1.33×10^{-6} Pa. Deposition rate was maintained as 10 nm/s using a quartz crystal balance, and the thickness of all films was set as 200 nm. The as grown WO_3 films were annealed at 500 °C for 1 h in oxygen atmosphere with temperature ramp of 2 ° C/min. The appearance of unannealed pristine film was reddish, after annealing its color changed to bluish.

The films were implanted with Ar^+ ions using electron cyclotron resonance based low energy ion implantation facility available at Inter University Accelerator Centre, New Delhi, India. The 100 keV Ar^+ ions were implanted into the WO_3 films with fluences ranging from 3×10^{15} to 1×10^{17} cm^{-2}. Surface morphology and elemental analysis of the material was studied using JEOL JSM6390LV secondary electron microscope (SEM) with the operating voltage 20 keV, equipped with Oxford INCA energy dispersive X–ray (EDX) spectrometer with resolution 4 nm. Working distance was set to 12 mm and image was taken in secondary electron image (SE) mode by the help of Everhart–Thornley SE detector. Crystallographic behavior of the films was examined at room temperature by a Bruker D8 Advance diffractometer using CuK_α radiation (1.54056 Å) at a continuous scan rate of 1°/min with resolution 0.1° for the range $20°\leq2\theta\leq60°$ and step size 0.02. The Raman measurements in backscattering geometry were carried out at room temperature by a Reinshaw Invia Raman microscope system using Ar laser (488 nm) as the excitation source with spectral resolution 0.21 cm^{-1}/pixel. The laser power focused onto the film was 0.25 mW. Optical transmittance spectra were measured using Shimadzu spectrophotometer (UV-2401 PC). Photoluminescence (PL) spectra were recorded using HORIBA PL spectrometer, where a xenon lamp was used as photon source. For gas sensitivity measurements, small pieces of prepared films with dimensions 1 cm × 1 cm were used. It was a two probe measurement, probes being fine copper wires of approx 0.05 cm diameter were

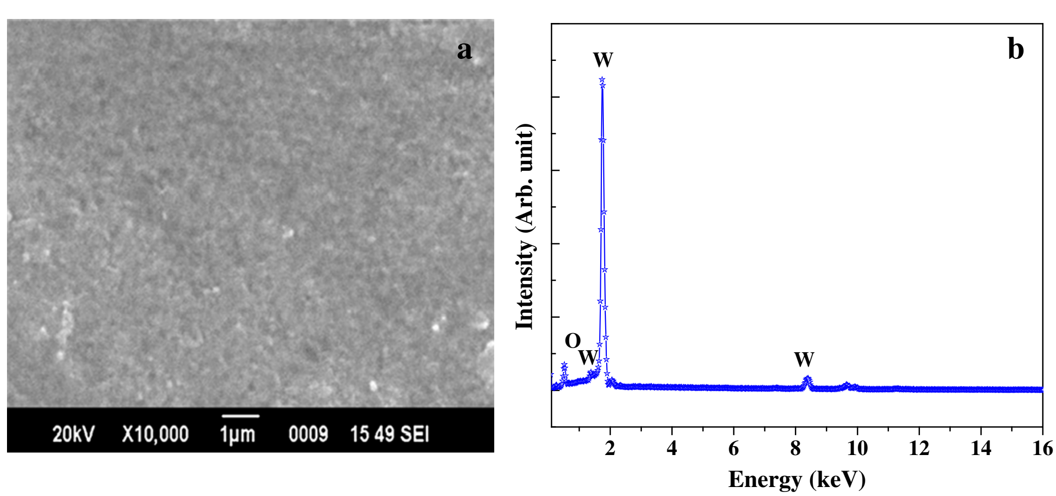

Fig. 2. (a) SEM image of pristine WO_3 film and (b) EDX analysis of same film.