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Effect of Ion Irradiation on Vanadium Oxide Thin Films Deposited by Reactive RF Sputtering Technique

Kapil Gupta, Sarvesh Kumar, Rahul Singhal

Abstract: ***Vanadium has many oxides (VO_2, V_2O_3, V_2O_4, V_6O_{13} and V_2O_5) due to high oxidation state. Properties of the vanadium oxide thin films can be changed by pressure, doping and strain. Ion irradiation can transform the phase, mix the two solid materials, form epitaxial crystallization and create nanostructure etc. in the materials. Purpose of our study was to observe the effect of swift heavy ions (SHIs) irradiation on vanadium oxide thin films. Thin films of vanadium oxide were deposited on the Si substrate by reactive RF sputtering technique. As-deposited thin films were irradiated by swift heavy ions (100 MeV Ag ions) at different fluences at room temperature. The effect of ions irradiation was studied by using grazing incidence X-ray diffraction (GIXRD), Fourier transform infrared spectroscopy (FTIR) and UV-vis-NIR spectrophotometer characterization techniques. GIXRD pattern revealed that swift heavy ions can induce the phase transformation (V_6O_{13} to V_2O_3) in the films. FTIR characterization showed that δ(V=O) stretching mode at 1020 cm^{-1} shifted to the lower wave number side. Optical properties showed blue shift in the absorption spectra at the higher fluences. These shifting are due to the lowering of vanadium's oxidation state in the thin films. This change in oxidation state of vanadium transforms the phase of the films. Irradiation with SHIs can transform the phase along with enhancement in the crystallinity of the vanadium oxide films.***

Keywords: ***Vanadium oxide, Reactive RF sputtering, Swift heavy ions***

I. INTRODUCTION

Transition metal oxides show correlated behavior, colossal magneto resistance and high temperature superconductivity. Morin [1] observed that titanium and vanadium oxides show a temperature driven reversible metal insulator transition. This transition also modifies the structural, electrical and optical properties of vanadium oxides and makes them interesting materials for various applications, such as electric/optical switching devices, smart windows, lithium-ion batteries etc [2]-[5]. Vanadium has many oxides due to high oxidation state (+4 and +5). Vanadium oxide thin films were deposited on different substrates by different deposition methods. It was found that stoichiometry of vanadium oxide thin films varies with deposition technique and process parameters, such as nature of substrate, substrate temperature, thickness of the film, oxygen concentration and nature of target material. Therefore it is very difficult to obtain a single phase, highly crystalline vanadium oxide thin films [6]-[10].

Crystalline phase and properties of vanadium oxide thin films can also be tuned by pressure, doping, annealing and ion bombardment. Effect of doping on optical properties of vanadium oxide films were studied by researchers [11], [12]. It was observed that doping with high valent cations decrease and low valent cation increase the switching temperature of electrical and optical properties of vanadium oxide thin films. Gupta and Kumar [13] deposited the thin films of vanadium oxide by RF sputtering and studied the effect of post annealing. It was found that a highly crystalline and layered structure vanadium pentoxide thin film obtained by post annealing at 500°C in Ar atmosphere. A highly oriented V_2O_5 thin film was deposited from inorganic solution on Si substrate. This film was converted in to VO_2 phase by reduction at temperature above 400°C by vacuum heating in a proper condition [14]. Proton irradiation [15] can also changes the properties of the VO_2 and V_2O_3 thin films. It was reported that vanadium or oxygen vacancies were responsible for the observed changes in the films. It was also suggested that oxygen stoichiometry has a vital role in alteration of the properties of vanadium oxide films.

Swift heavy ions (SHIs) irradiation is a versatile tool to create high pressure, high temperature and defects in a controlled manner in the material [16], [17]. High energy deposited by SHIs irradiation in the thin films [18] may also be used for dramatic alternation in the structure and composition (amorphization and phase formation). SHIs irradiation (180 MeV Kr) on iron thin films deposited on Si substrate induce an oxide phase formation on the iron surface due to the diffusion of oxygen [19]. Gupta et al. [20] studied the results of swift heavy ions irradiation on the vanadium oxide thin films. They deposited the films by PLD technique on the Si (100) substrate and irradiated the films with Au ions (energy 200 MeV) at different fluences. It was found that high energy ions changed the transition properties of the films drastically.

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* Correspondence Author
Kapil Gupta*, Department of Physics, Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Sector-43, Faridabad – 121001, India. Email: kapil1809@gmail.com
Sarvesh Kumar, Department of Physics, Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Sector-43, Faridabad – 121001, India. Email: guptask10@gmail.com
Rahul Singhal, Department of Physics, Malaviya National Institute of Technology, JLN Marg, Jaipur-302017, India. Email: rsinghal.phy@mnit.ac.in

Swift heavy ions irradiation introduces defects around the ion track region, which can change the electrical and structural properties of the thin films. Kokabi and Studer [21] studied the sensitivity of high energy (6 GeV) Pb ions on the $(V_{1-x}Cr_x)_2O_3$ ceramics. Modification in the electrical properties with the thermal variation showed that influence of high energy was more prominent in the semiconducting phase in comparison to metallic phase. Hofsass et al. [22] deposited the 100 nm thin film of vanadium dioxide from V_2O_5 target by RF magnetron sputtering on Si and observed the shift in the transition temperature and tuning of the conductivity of the sample by the irradiation with 1 GeV U ions.

Mostly researchers used vanadium solid target as a target material for the deposition of vanadium oxide thin films. We are using vanadium pentoxide powder, the cost of powder is very low in comparison to the solid sputtering target. In present work, we deposit the vanadium oxide thin films on silicon substrate by reactive RF sputtering using V_2O_5 powder pellet as a target material and studied the effect of swift heavy ions (100 MeV Ag ions) irradiation on the films at different fluences.

II. MATERIALS AND METHOD

Thin films of vanadium oxide (~200 nm) were fabricated onto the Si substrate by reactive RF sputtering at MNIT, Jaipur. Vanadium pentoxide (V_2O_5) powder (purity 99.9%) was crushed and pressed under the pressure of 10×10^6 Pa to make pellet of 2 mm thick and 50 mm diameter in size. This pellet was sintered for 2 hours at 400°C as the melting point of vanadium pentoxide is low (~650°C). The sintered pellet was used as a target for reactive RF sputtering setup. Trichloroethylene and acetone were used to clean silicon substrates in ultrasonic cleaner for 15 minute, after that the substrates were rinsed by deionized water thoroughly. Sputtering was carried out in argon-oxygen atmosphere (99.25 SCCM argon and 0.75 SCCM oxygen) at working pressure 2.0×10^{-2} mbar, RF power 120 Watt, substrate temperature 500°C, and deposition time around 1.5 hours. Films thickness was measured during deposition by thickness monitor.

Irradiation of the as-deposited films with 100 MeV Ag ions at different fluences (1×10^{11}, 5×10^{11} and 5×10^{12} ions/cm^2) at room temperature was performed in the material beam line at IUAC, New Delhi. The as-deposited and irradiated films were analyzed to study the structural properties by Grazing Incidence X-ray Diffraction (GIXRD). The GIXRD measurements were done by using Bruker D advance X-ray diffractometer and the wavelength of X-ray was 0.154 nm (CuK α). Fourier Transform Infrared Spectroscopy (Bruker Tensor 37) was performed to examine the infrared transmittance of the films. Optical properties were studied by UV-vis-NIR spectrophotometer (lambda 750 UV/Vis/NIR Spectrophotometer).

III. RESULTS AND DISCUSSION

Electronic energy loss and nuclear energy loss of swift heavy ions in vanadium oxide thin films are calculated by SRIM program. For 100 MeV Ag ions the electronic energy loss in vanadium oxide (V_2O_5) is 1231 eV/Å and the nuclear energy loss is about 6.29 eV/Å. Figure 1 depicted the GIXRD patterns of the films (as-deposited and irradiated), peaks at 26.53° and 35.2° corresponds to (060) and (331) planes of the V_6O_{13} orthorhombic structure (JCPDF card no 78-0983). Strain produced at the time of film deposition may slightly displace the peaks positions. Broad peak around 55.90° may correspond to SiO_2 layer and strongest peak at 54.13° may be due to the substrate. In the irradiated films, it has been observed that at low fluence (1×10^{11} ions/cm^2) peaks are at 24.07°, 33.0°, 43.38° and 51.55° and as we go to higher fluences (5×10^{11} and 5×10^{12} ions/cm^2), they are slightly shifted to higher 2θ sides. Stress produced at higher fluences by the SHIs irradiation may switch the peaks positions [23]. Peaks around 24.5° and 33.2° are due to the (012) and (211) plane of V_2O_3 phase and the peak at 43.8° is of the (222) plane of V_4O_7 phase.

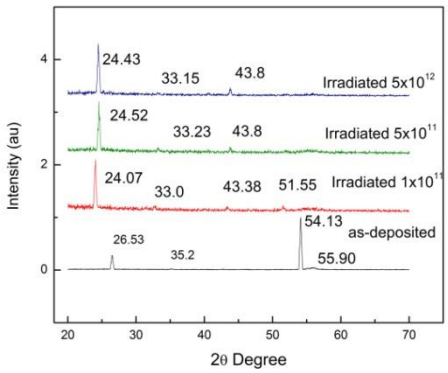

Fig. 1 GIXRD patterns of as-deposited and irradiated films

We also observed that at 5×10^{12} ions/cm^2 fluence, intensity of peak at 43.8° is increased. This may be due to the rise in the crystallinity of the films after irradiation. Also peak due to substrate is not appeared in the irradiated samples. This may be due to the formation of amorphous SiO_2 phase by the irradiation. The observed results showed that ions irradiation transform the phase of the as-deposited films. A similar phase formation was observed in NiO/Si system irradiated by SHIs [24] at higher fluence (5×10^{14} ions/cm^2). Diffusion of oxygen took place from substrate to film and film to chamber without disturbing the vacuum of the chamber, when CuO thin films irradiated by 210 MeV I ions [25].

In order to understand the micro structural changes in the films, FTIR characterization were done in the range from 400 to 1500 cm^{-1} as shown in figure 2. In the spectrum, wide band at 505 cm^{-1} is attributed to the stretching mode of oxygen shared by three vanadium atoms and peak at 607 cm^{-1} is related to the stretching V-O_B-V bridging group with different strength [9].

Broad band at 935 cm^{-1} is due to Si substrate in case of as-deposited films. In case of irradiated samples, at low fluence (1×10^{11} ions/cm^2) bands at 611 cm^{-1} and 740 cm^{-1} are originated from ν(V-O) bond and band appears at 1020 cm^{-1} is attributed to δ(V=O) stretching mode. The stretching vibration of vanadium dioxide due to V-O-V band is responsible for the band at 664 cm^{-1}. At higher fluence (5×10^{11} and 5×10^{12} ions/cm^2) δ(V=O) stretching mode tend to shift to lower wave number side i.e. from 1020 cm^{-1} to 950 cm^{-1}.

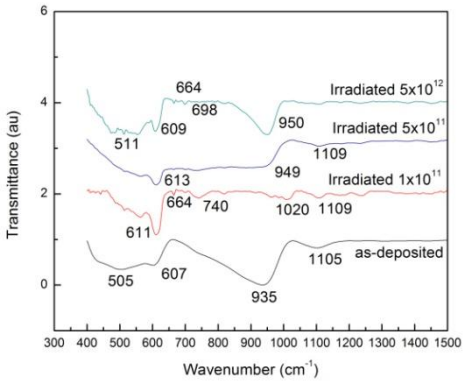

Fig. 2 FTIR patterns of as-deposited and irradiated films

This shifting of the band towards the lower wave number is due to the lowering of the oxidation state of vanadium atoms and weakness of the V=O bond [26]. The observed results revealed that swift heavy ions irradiation can do the reduction of the vanadium species in vanadium oxide thin films.

Optical reflectance of the irradiated films in the range from UV to NIR is revealed in figure 3. At low fluence (1×10^{11} ions/cm^2) a valley is observed near 300 cm^{-1} along with some ripples and at higher fluence the spectra revealed significantly blue shift in optical absorption edge [27] in the wavelength region 250 to 700 nm along with improvement in density of ripples.

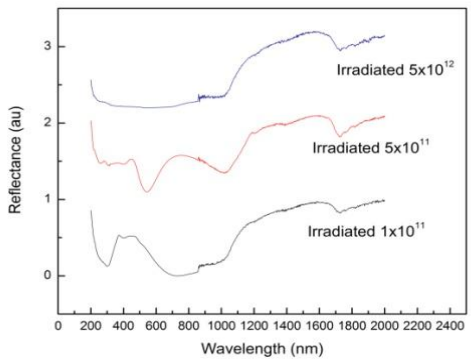

Figure 3 UV-vis-NIR spectra of irradiated films

IV. CONCLUSION

Thin films of vanadium oxide were deposited by reactive RF sputtering method by using V_2O_5 powder as the source material. The as-deposited films were irradiated with 100 MeV Ag ions. GIXRD characterization revealed that as-deposited films were oriented along (003) plane of V_6O_{13} phase. After irradiation the phase of the films change (V_6O_{13} to V_2O_3) and films were oriented along the (012) plane of V_2O_3. FTIR spectra also suggest that δ(V=O) stretching mode tends to shift to lower wave number i.e. from 1020 cm^{-1} to 950 cm^{-1}. This shifting of band towards the lower wave number side is because of the lowering of oxidation state of vanadium atom or diffusion of oxygen atoms due to the irradiation with swift heavy ions. SHIs irradiation can change the vanadium's oxidation state and transform the phase of as-deposited vanadium oxide thin films. These changes may be due to transiently molten cylindrical zone created by the passage of swift heavy ions in the material.

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AUTHORS PROFILE

Mr. Kapil Gupta, is a research scholar in Department of Physics, Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Faridabad. He has completed master degree in Physics from MDU, Rohtak. His research area is material science and he started working on deposition of vanadium oxide thin films by various techniques and swift heavy ions irradiation.

Dr. Sarvesh Kumar, is currently working as Associate Professor at Department of Physics, Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Faridabad. He has completed Ph.D. in Physics from Dr. B. R. Ambedkar, University, Agra. He has visited Institut fuer Strahlenphysik, Stuttgart, Germany and Hahn-Meitner-Institut fuer Kernforschung, Berlin, Germany, under DST-DAAD exchange programme. Two Ph.D. students have completed their doctoral degree under him and another three are on-going.

Dr. Rahul Singhal, is currently working as Assistant Professor at Department of Physics, Malaviya National Institute of Technology Jaipur. He has completed master degree in Physics from IIT Roorkee and PhD in Materials Science from Jawaharalal Nehru University New Delhi. He has worked as DST INSPIRE Faculty and CSIR- Nehru Science Fellow at National Physical Laboratory New Delhi. He did Post-Doc from North Carolina State University, Raleigh USA under the prestigious American Physical Society Fellowship. He has published more than 90 paper in reputed international journals like ACS Energy Letters (impact factor: 12.6), RSC-Journal of Materials Chemistry A (impact factor- 9.5) etc. Four Ph.D. students have completed their doctoral degree under him and another two are on-going.