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 (VO₂, V₂O₅, V₂O₅₂, and V₂O₃) 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, the 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 (V₂O₅ to V₂O₃) 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.

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Effect of ion irradiation on vanadium oxide films can be used for dramatic alternation in the structure and composition (amorphization and phase formation). Hofsass et al. [15] can also changes the properties of the VO₂ and V₂O₅ 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 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) substrates and irradiated the thin film with Au ions (energy 200 MeV) at different fluences. They found that high energy ions changed the transition properties of the films drastically. 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 (V₁₋ₓCrₓ)₂O₃ 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.
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[22] deposited the 100 nm thin film of vanadium dioxide from V$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$) powder (purity 99.9%) was crushed and pressed under the pressure of 10$\times$10$^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$\times$10$^{-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$\times$10$^{11}$, 5$\times$10$^{11}$ and 5$\times$10$^{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$\alpha$). 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$_2$O$_5$) 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 (006) and (331) planes of the V$_2$O$_5$ 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$\times$10$^{11}$ ions/cm$^2$) peaks are at 24.07°, 33.0°, 43.38° and 51.55° and as we go to higher fluences (5$\times$10$^{11}$ and 5$\times$10$^{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$_2$O$_5$ phase and the peak at 43.8° is of the (222) plane of V$_2$O$_7$ phase.

![Fig. 1 GIXRD patterns of as-deposited and irradiated films](image)

We also observed that at 5$\times$10$^{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$\times$10$^{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 305 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$_{bridging}$ 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$\times$10$^{11}$ ions/cm$^2$) bands at 611 cm$^{-1}$ and 740 cm$^{-1}$ are originated from v(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$\times$10$^{11}$ and 5$\times$10$^{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$^{-1}$.
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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VI. REFERENCES
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