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STUDY OF THE EFFECT OF ANNEALING AND IRRADIATION OF HIGH ENERGY IONS ON VANADIUM OXIDE THIN FILMS

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ABSTRACT

Vanadium due to multiple oxidation states (+2 to +5) has various oxides like vanadium dioxide, vanadium pentoxide, and hexavanadium tredecaoxide. Thin films of vanadium oxide have been fabricated using the reactive radio frequency sputtering technique. Deposited films are then annealed in Argon (Ar) environment at 500°C and then irradiated with 100 MeV Ag^{8+} high-energy ions. The vibrational properties of the thin films have been analyzed by Raman scattering and Fourier transform infrared spectroscopy (FTIR). Results (Raman and FTIR spectra) of the annealed film show that the V_6O_{13} phase is converted into a mixed phase (V_6O_{13}, VO_2, and V_2O_5). The annealed irradiated film shows no change in the Raman lines while a shift towards the lower wave number is noticed in FTIR spectra peaks. This shifting of peaks towards lower wave numbers in FTIR spectra is attributed to the weakening of vanadium oxygen bonds. It is considered that the weakening of bonds could occur when high-temperature cylindrical zones are created along the ion track.

Keywords: Annealing, Vanadium Oxide, High Energy Ions, Thin Films.

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INTRODUCTION

Vanadium oxides are one of the most interesting correlated electron systems that have been studied by various researchers. Characteristic features of films can be altered by stress, annealing, low or high-energy ion irradiation, and strain. Vanadium oxide thin films show fascinating properties due to which, they have many potential applications.[1-3] It is always a challenging job for researchers to grow a single-phase vanadium oxide film. Thin films can be grown by various chemical and physical deposition techniques, like sol-gel, sputtering[4], pulsed laser evaporation, e-beam evaporation, chemical spray pyrolysis[5], etc. Vanadium oxide thin films were fabricated on fused silica from V metal targets by RF sputtering. The parameters of deposition were set as a target substrate distance of 6.0 cm, RF power of 120 Watts, and substrate temperatures of 400-480°C. Micro Raman results revealed that annealed film consisted of three regions, a yellow region (vanadium dioxide) black region (hexavanadium tredecaoxide), and a white amorphous region.[6] Oxygen concentration during the deposition of vanadium films is a pivot as vanadium (V) contains multiple oxidation states. The effect of O_2 concentration varying from 1% to 7% has also been studied on the VO_x films fabricated by reactive radio frequency sputtering from the V target.[7] It was found that the film deposition rate depended on the oxygen concentration and the films deposited at 2% O_2 concentration contained a VO_2 phase. Various stoichiometric films were obtained by oxidation and reduction of the films by annealing. The occurrence of multiple-phase transition has been reported when thin films of vanadium oxide are heated from room temperature to 550°C.[8] Characterization results show that the thin film undergoes many phase transitions, i.e., VO_2, V_6O_{13}, V_3O_7, and V_2O_5 along with the change in conductivity as the temperature increases. This may be assigned to the absorption of oxygen at higher temperatures and at 550°C stable V_2O_5 phase is obtained. VO_2 thin films developed on Al_2O_3 and Si substrate from V target were studied and an intermediate phase (between monoclinic and tetragonal phase) appeared in the films deposited on Al_2O_3. No such phase was formed in Si substrate films.[9] The origin of the intermediate phase was due to the strained structure of films deposited on Al_2O_3.

Gupta *et al.* (2017) studied the annealing effect on vanadium oxide thin films.[10] The sintered pellet of vanadium pentoxide powder was used for the deposition of films on a heated Si substrate (temperature

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300°C). GIXRD results depicted that post-annealing transforms the amorphous phase of vanadium pentoxide into a crystalline phase. It was reported that irradiation with high-energy particles alerted the properties of the vanadium oxide thin films.[11] Diffusion of oxygen in CuO thin films by high energy (210 MeV) I ions was observed by Avasthi *et al.* Films were irradiated at different fluences and observed that oxygen diffusion took place from the film to the vacuum chamber. This was explained on the basis of the transient thermal effect created by swift heavy ions (SHIs) along its path in the film. Vanadium pentoxide (V_2O_5) films were irradiated with Ag ions (energy 200 MeV) at room temperature. SHIs induced amorphization of the film due to transient thermal effect and created oxygen vacancies. Suppression in Raman spectra, change in electrical properties and red shifting in band gap were explained by the oxygen vacancies created by swift heavy ions (SHIs).[12] In the present work, thin films of vanadium oxide are deposited from the sintered pellet of V_2O_5 powder (source material) by the reactive RF sputtering method. The effects of post-annealing and irradiation of high-energy ions on deposited samples have been studied.

EXPERIMENTAL

Vanadium oxide thin films of thickness about 200 nm were deposited by reactive radio frequency sputtering setup. The sintered pellet of V_2O_5 powder of purity 99.9% was used as source material. Si substrates were used for the deposition of films. Deposition parameters were discussed in detail in our previous work.[13] RF sputtered samples were annealed at 500°C temperature in presence of Argon for 1 hour and films were cooled in the same environment. These films were irradiated with high-energy Ag^{8+} ions (100 MeV) at different fluences (1×10^{11}, 5×10^{11}, and 5×10^{12} ions/cm^2). To examine the vibrational modes, Raman scattering measurement was characterized by "Airix corp, STR 500, system, with a high resolution < 0.5 cm^{-1} and wavelength 532 nm". Infrared transmittance (IR) of the films was performed by Perkin Elmer spectrum-2 setup at MNIT, Jaipur.

RESULTS AND DISCUSSION

Raman Result

Raman scattering (RS) spectroscopy is used as a tool in solids, liquids, and gases in order to determine existing rotational and vibrational modes of the molecules in the materials. Raman scattering (RS) spectra of films deposited by RF sputtering (as-deposited and annealed) are shown in Fig.-1. The spectrum of the deposited film shows lines at 134, 302, and 521, and a plateau near 955 cm^{-1} is observed which is to vanadyl stretching vibration mode (V-O_v).[14] The line at 134 cm^{-1} corresponds to the bending vibration of O-V bonds and 302 cm^{-1} corresponds to three coordinated O-V_3 bonds. These modes belong to the hexavanadium tredecaoxide (V_6O_{13}) phase of vanadium oxide and the line at 521 cm^{-1} is due to Si.[15] In the spectra of annealed film, a new line at 827 cm^{-1} of small intensity is observed which is due to the VO_2 phase.

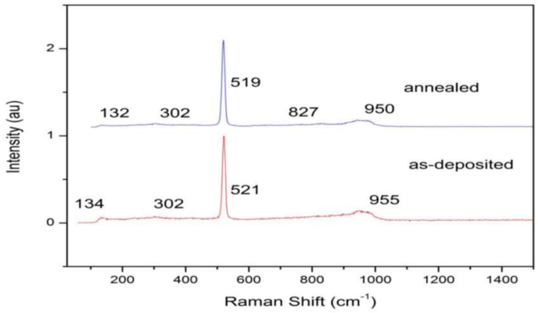

Fig.-1: RS Spectrum of RF Sputtered and Ar Annealed Thin Films

A Raman spectrum of annealed irradiated films is shown in Fig.-2, where no new lines are observed at different fluences. It has been observed that the vibrational modes of V_2O_5 and V_6O_{13} are similar, due to their structural unit and layered structure.

FTIR Result

FTIR characterization of RF sputtered and argon annealed films are shown in Fig.-3. RF sputtered film spectrum show, a broad peak at 505 cm^{-1} corresponds to the stretching mode of oxygen shared by three vanadium atoms, peak at 607 cm^{-1} is attributed to stretching V-O$_B$-V bridging group of different strength.[16] The wide peak at 935 cm^{-1} is due to underlying Si.

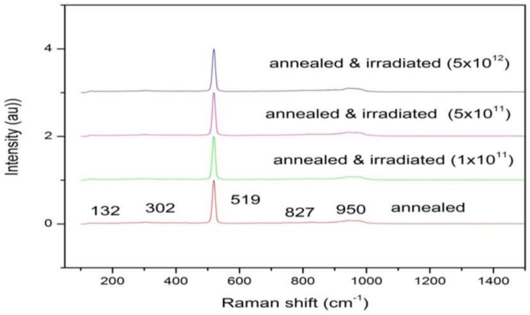

Fig.-2: RS Spectrum of Ar Annealed and High Energy Irradiated Films

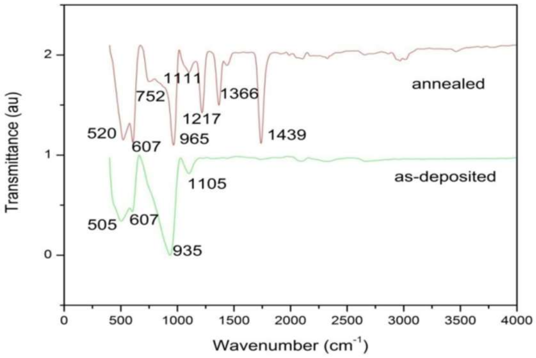

Fig.-3: IR Spectra of RF Sputtered and Ar Annealed Films

In the IR spectra of annealed samples, new bands are observed at 520, 607, 752, and 965 cm^{-1} peaks. Peaks at 752 and 965 are attributed to asymmetric stretching of V-O$_b$-V mode and stretching of ν(3V-O$_C$) mode of vanadium pentoxide respectively.[17,18] Peak appearing at 520 is due to the VO$_2$ phase.[19] In FTIR spectra of annealed irradiated films (in Fig.-4), it is observed that at low fluence, peaks at 752 and 965 cm^{-1} of the annealed film are shifted towards the lower wave number side.

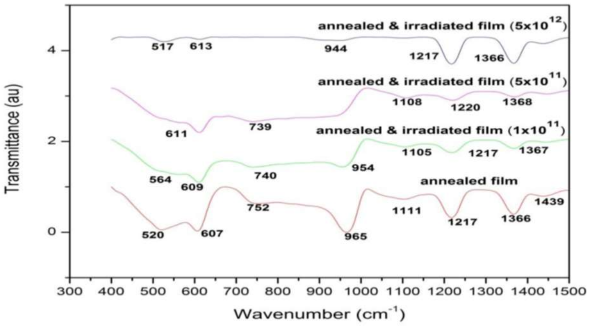

Fig.-4: IR Spectra of Ar Annealed and High Energy Irradiated Films

The decrease in intensity of the bands with an increased influence is also reported. This frequency shift of the modes is due to the weakening of V=O bonds in the film.[20]

CONCLUSION

To summarize, we have synthesized the RF sputtered films of vanadium oxide on a Si substrate. These RF sputtered films are annealed and then irradiated with high energy 100 MeV Ag^{8+} ions at different fluences. It is observed that the V$_6$O$_{13}$ phase is obtained from reactive RF sputtering, this phase is converted into a mixed phase (V$_6$O$_{13}$, VO$_2$, and V$_2$O$_5$) by post-annealing. In Irradiation of annealed films, results show that peaks are shifted towards the lower wave number side and the intensity of peaks also decreases with fluence. These shifts are due to the weakening of V=O bonds. High-energy ions interact with matter and deposit their energy either by ionization or electronic excitation of the material. The electronic energy loss for 100 MeV Ag^{8+} ions is much more than the nuclear energy loss. It is considered that the weakening of bonds could occur when high-temperature cylindrical zones are created along the ion track. Thus, the observed changes in the film may be assigned to electronic energy loss.

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