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Structural Stability and Optical Band Gap Modification in V_2O_5 Thin Films via H_2^+ Ion Implantation

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Abstract

This study examines the structural and optical modifications in vanadium pentoxide (V_2O_5) thin films due to thermal annealing and hydrogen ion (H_2^+) implantation. X-ray diffraction (XRD) analysis indicates that the orthorhombic phase remains intact following implantation at different fluences of 1×10^{12}, 1×10^{13}, and 1×10^{14} ions/cm^2. The average grain size exhibits an increase to 63.2 nm at lower fluences, followed by a decrease to 18.1 nm at the highest fluence. This observation suggests a complex relationship between ion energy and grain growth dynamics. Fourier-transform infrared (FTIR) spectroscopy indicates peak broadening and a decrease in crystallinity as fluence increases, which suggests structural degradation. UV-Vis spectroscopy indicates a reduction in absorbance attributed to defect formation, accompanied by an increase in the optical band gap from 3.34 eV to 3.53 eV as fluences rise. The results indicate that controlled H_2^+ implantation is an effective method for tailoring V_2O_5 thin films, making them suitable for optoelectronic and energy storage applications.

Keywords: Vanadium pentoxide; Thermal annealing; Hydrogen ion implantation; Structural modifications; Optical band gap

Introduction

Ion implantation has become a crucial method for altering the structural and optical characteristics of vanadium pentoxide (V_2O_5) thin films, which are increasingly important in a range of applications, such as electronics and optoelectronics [1-3]. This method entails subjecting materials to ion bombardment, which facilitates meticulous regulation of doping concentrations and the formation of defects. The accuracy of this process is essential for customizing the electronic and optical features of V_2O_5, a wide-bandgap semiconductor known for its distinctive properties.

The structural changes caused by ion implantation are mainly associated with the creation of defects and oxygen vacancies, which can greatly modify the crystal phase and morphology of V_2O_5 films. For instance, investigations indicate that nitrogen ion implantation results in a preferential formation of β-V_2O_5 instead of α-V_2O_5, accompanied by improved crystallinity and a decrease in defects when properly optimized [4]. The existence of oxygen vacancies plays a significant role in enhancing the material's conductivity and influences its optical band gap, thereby enabling alterations in its photonic responses [5]. Furthermore, recent studies on metal ion implantation, particularly gold, have revealed the capability of forming nanocrystalline clusters within V_2O_5 matrices, influencing both structural integrity and electrical performance [6]. This holds considerable importance since the level of ion fluence during implantation is directly linked to the structural evolution and phase transitions occurring within the V_2O_5 films. The development of distinct crystalline phases under varying implantation conditions highlights the versatility of V_2O_5 for targeted functional applications [2].

Moreover, the influence of ion implantation goes beyond mere structural changes; it is also essential in fine-tuning the optical characteristics of V_2O_5 films. For example, the band gap of V_2O_5 has been demonstrated to shift with different ion fluences, reflecting alterations in the electronic structure caused by defect formation and changes in the crystalline lattice [2,3]. Research has shown that ion implantation can result in a narrowing of the band gap, improving the material's absorption properties in the visible spectrum, which is beneficial for uses in solar cells and photodetectors. Furthermore, studies show that the optical absorption spectra can uncover transitions associated with defect states in the band structure, highlighting the intricate relationship between ion implantation and the optical properties of V_2O_5. These insights enhance our comprehension of the material's properties and facilitate the creation of innovative applications in advanced optoelectronic devices.

Materials and Methods

Thin films of vanadium pentoxide (V_2O_5) were deposited on glass substrates through thermal evaporation within a vacuum environment. The deposition process entailed the evaporation of 99.9% pure V_2O_5 from a small tungsten boat while maintaining the chamber pressure at 5×10^{-6} mbar. The films produced exhibited a thickness of 500 nm. Following deposition, the films were subjected to thermal annealing at 500°C for a duration of 6.5 hours. The annealing temperature was systematically raised from 100°C to 500°C in ambient air pressure to promote crystallization. After crystallization, the V_2O_5 films underwent 20 keV hydrogen (H_2^+) ion implantation utilizing a tabletop accelerator at the Inter-University Accelerator Centre, New Delhi, India. The implantation was executed using ion fluences that varied from 1×10^{12} to 1×10^{14} ions/cm^2. X-ray diffraction (XRD) was conducted to examine the structural phase of both annealed and implanted films, utilizing a Rigaku Miniflex 600 diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 20 mA. FTIR analysis was performed utilizing a Shimadzu IR Infinity spectrometer in KBr mode, spanning the 400–4000 cm^{-1} range. The optical properties and bandgap of the thin films were analyzed utilizing a UV-vis-NIR spectrophotometer (Model: Shimadzu 3600i Plus) at the Central University of Jammu, Jammu.

Results and Discussion

XRD Study

Figure 1 shows the X-ray diffraction (XRD) patterns for the structural analysis of V_2O_5 thin films deposited on glass substrates after thermal annealing at 500°C for 6.5 hours, followed by hydrogen ion (H_2^+) implantation at different fluences. The films display distinct, well-defined diffraction peaks, demonstrating their crystalline characteristics. The diffraction peaks align with the orthorhombic phase of V_2O_5, consistent with JCPDS card No. 01-077-0050 [2]. The characteristic peaks are observed at 2θ values of approximately 18°, 24.9°, 27.62°, and 32.50°, corresponding to the (211), (301), (202), and (312) planes of the V_2O_5 orthorhombic structure. The consistency of these peaks in both the annealed and ion-implanted samples indicates that the fundamental crystal structure of V_2O_5 is preserved, even in the presence of ion implantation.

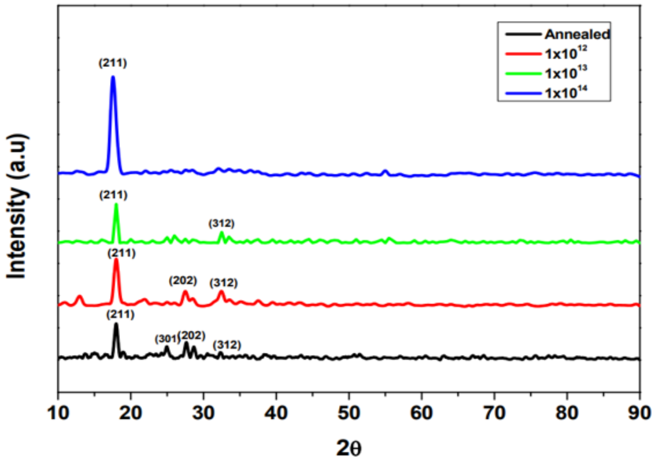

Figure 1: *XRD Patterns of V_2O_5 Thin Films of Different Ion Fluences.*

The crystalline structure's stability in the ion-implanted samples indicates that the relatively light hydrogen ions do not cause substantial disruption to the crystal lattice. Following implantation at fluences of 1×10^{12}, 1×10^{13}, and 1×10^{14} ions/cm^2, the diffraction peaks remain aligned with those observed in the annealed sample. This indicates that hydrogen ion implantation, in this instance, does not cause significant structural changes, maintaining the overall orthorhombic characteristics of the V_2O_5 films. The observation of extra minor peaks in the annealed sample at 2θ values related to the (301) and (202) planes underscores the stability and refinement of the crystal structure prior to ion implantation. The Debye-Scherrer formula provides a calculation for determining crystallite size, further substantiating this interpretation as follows:

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where 'D' is the crystallite (grain) size, β is the full width at half maximum (FWHM) of a diffraction peak with θ angle, and λ = 1.5405 Å is the X-ray wavelength.

Table 1 shows the variation of the crystallite size with ion fluence. The difference in grain size observed between the annealed and ion-implanted V_2O_5 samples indicates a distinct influence of ion implantation on the microstructure of the material. The annealed V_2O_5 film exhibits a grain size of approximately 24.7 nm, determined through the application of the Debye-Scherrer formula. Nonetheless, the ion-implanted samples reveal a clear pattern: at reduced fluences (1×10^{12} and 1×10^{13} ions/cm^2), the grain size markedly increases to 54.8 nm and 63.2 nm, respectively, whereas at the maximum fluence (1×10^{14} ions/cm^2), the grain size declines significantly to 18.1 nm. The observed trend can be elucidated through the interaction of ion implantation with the crystallization process, which affects grain growth in various manners based on the ion fluence applied. At lower fluences, the energy delivered by the implanted ions encourages dynamic annealing and reordering within the material, aiding in grain growth [7]. The ions create defects and displacements within the lattice; however, the energy levels remain insufficient to induce significant damage [8]. In contrast, these defect sites serve as nucleation points that facilitate the coalescence and growth of grains, leading to larger grain sizes when compared to the annealed sample [9].

As the fluence increases, the dynamics undergo a transformation. At the maximum fluence of 1×10^{14} ions/cm^2, the energy and density of the ions reach levels that are adequate to create a greater density of defects, initiating the fragmentation of the grains. This procedure results in a reduction of the overall grain size to 18.1 nm, which is smaller than the sizes observed in both the annealed and low-fluence ion-implanted samples. The elevated ion energy significantly disturbs the lattice, surpassing the dynamic annealing effects that had earlier facilitated grain growth. This leads to a scenario in which grain fragmentation starts to prevail over grain growth, resulting in a decrease in grain size [10].

***Table 1:** Variation of Average Grain Size with Fluence.*

Fluence (ions/cm^{-1})	Average Grain Size (nm)
0	24.7
1x10^{12}	54.8
1x10^{13}	63.2
1x10^{14}	18.1

FTIR Study

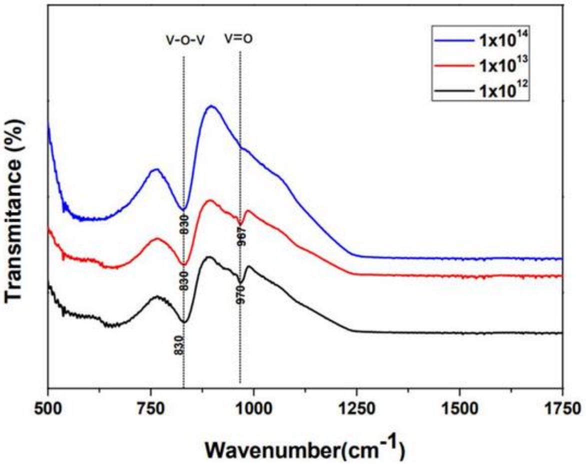

***Figure 2:** FTIR Spectra of V_2O_5 Thin Films at Different Ion Fluences.*

Figure 2 shows the FTIR spectra of V_2O_5: Gl thin films after the 20 keV H_2^+ ion implantation at varying fluences (1x10^{12}, 1x10^{13}, and 1x10^{14} ions/cm^2). The peaks corresponding to the V=O bond (~885 cm^{-1}) and the V-O-V bond (~626 cm^{-1}) suggest significant structural alterations in the material [11]. With an increase in ion fluence, the FTIR spectra indicate a pattern of structural degradation. At the lowest fluence of 1x10^{12} ions/cm^2, the peaks are distinctly defined, suggesting a more crystalline and organized structure. This indicates that the material maintains a largely preserved crystal lattice with a reduced number of defects resulting from the ion implantation [12]. The distinctness of the V=O and V-O-V bond peaks indicates a material that has preserved a significant degree of its original crystallinity. With an increase in fluence to 1x10^{13} ions/cm^2, the peaks exhibit broadening, indicating a degradation in the crystal structure. The process of ion implantation at this fluence leads to the introduction of a considerable quantity of defects, including vacancies and dislocations, which disrupt the long-range order of the crystal lattice. The broadening of the FTIR peaks indicates a reduction in crystallinity and an increase in structural disorder. The material is undergoing a transition from a crystalline structure to a more amorphous state due to the accumulation of damage.

At the maximum fluence of 1x10^{14} ions/cm², the FTIR peaks exhibit the broadest and least defined characteristics. This additional expansion indicates that the material has undergone considerable structural deterioration. The elevated fluence of H_2^+ ions results in greater lattice damage, and the dynamic annealing effects, which may alleviate some damage at reduced fluences, are surpassed. The crystal lattice exhibits significant disorder, leading the material to resemble an amorphous state. The significant loss of peak sharpness and the overall reduction in structural integrity are clearly demonstrated in the degraded FTIR spectra. The FTIR spectra indicate that a higher fluence of H_2^+ ions results in gradual structural degradation of V_2O_5: Gl thin films. The material exhibits a relatively high degree of crystallinity at low fluence, but as the ion fluence rises, it transitions to a more amorphous state. This is evidenced by the broad and less defined FTIR peaks, which suggest an increase in disorder.

Uv-Vis Spectroscopy Study

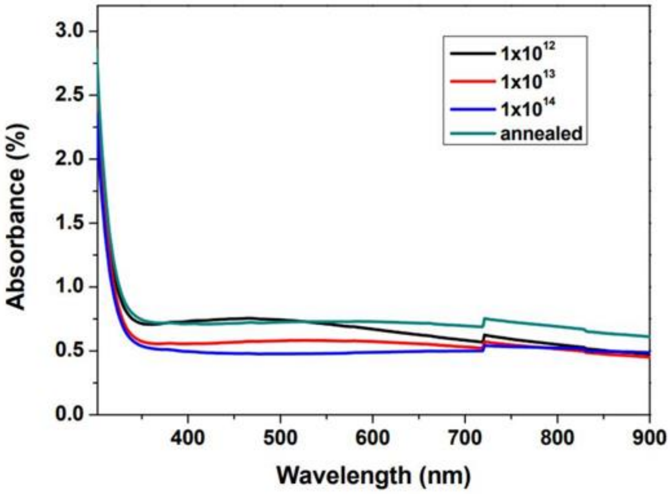

***Figure 3:** UV-Vis Absorbance Spectra of Pristine and N^+ Implanted V_2O_5 Thin Films at Different Fluences.*

Figure 3 illustrates the absorbance spectra of V_2O_5 thin films within the UV-visible wavelength range (300 to 900 nm) for different hydrogen ion (H_2^+) fluences, including a sample that has undergone annealing. The pristine annealed sample shows the highest absorbance, especially in the UV region below 400 nm, suggesting optimal electronic transitions that facilitate effective light absorption. The increased absorbance indicates a well-ordered crystal structure and a low defect density in the annealed V_2O_5 film. With the increase in ion fluence from 1x10^{12} to 1x10^{14} ions/cm², there is a significant reduction in absorbance observed throughout the spectra. The decrease can be linked to multiple factors, such as the creation of defects and disorder within the crystal lattice resulting from ion implantation. The introduction of defects can lead to the scattering of incoming light, thereby diminishing the effective absorption of photons. Furthermore, alterations in crystallinity and surface morphology resulting from ion bombardment influence the electronic states that govern light absorption, resulting in a reduction in absorbance. Even with these alterations, the general trends in absorbance stay consistent throughout the samples, indicating that although ion implantation affects the absorbance properties, the core optical characteristics of V_2O_5 remain largely stable.

Figure 4 (a-d) presents the Tauc plots for V_2O_5 thin films subjected to different hydrogen ion (H_2^+) fluences, enabling the determination of the optical band gap. The Tauc plot is created by plotting the $(\alpha h\nu)^2$ (where α is the absorbance and $h\nu$ is the photon energy) against photon energy $h\nu$. This approach facilitates the identification of the optical band gap through the linear extrapolation of the graph. The band gap of the pristine V_2O_5

sample measures around 3.34 eV. The band gap exhibits a gradual increase with rising fluence: 3.40 eV at a fluence of $1x10^{12}$ ions/cm^2, 3.50 eV at $1x10^{13}$ ions/cm^2, and 3.53 eV at $1x10^{14}$ ions/cm^2. The observed increase in the band gap is certainly associated with the formation of defects. The introduction of defects from ion implantation can create localized states in the band structure, potentially altering the energy levels accessible for electronic transitions. Such defects can also induce alterations in the material's overall electronic environment, potentially stabilizing elevated energy levels that are associated with enhanced band gap values. Consequently, although ion implantation creates disorder, it can also improve specific structural features, leading to enhanced optical properties at elevated fluences.

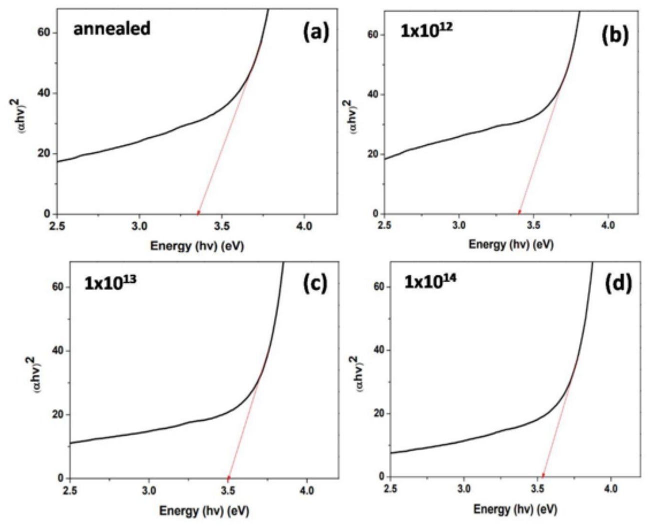

Figure 4: *Tauc Plot for Direct Band Gap.*

Conclusion

In conclusion, this study provides a thorough analysis of the effects of thermal annealing and hydrogen ion (H_2^+) implantation on the structural and optical characteristics of V_2O_5 thin films. The results indicate that the orthorhombic phase of V_2O_5 maintains stability at different ion fluences, suggesting that hydrogen ion implantation does not considerably affect the crystalline structure. The variation in average grain size indicates a complex relationship between ion fluence and microstructural evolution, characterized by an initial increase at lower fluences and a subsequent significant decrease at the highest fluence levels. This behavior indicates that lower ion fluences facilitate dynamic annealing and grain growth, whereas higher fluences result in an increased density of defects, causing grain fragmentation. FTIR analysis supports these findings, demonstrating structural degradation with increasing ion fluence, resulting in a transition of the material from a more crystalline state to a less ordered, amorphous form. Additionally, UV-Vis spectroscopy indicates a reduction in absorbance linked to defect formation, while the noted increase in the optical band gap from 3.34 eV to 3.53 eV implies that ion implantation may improve certain optical properties, even in the presence of disorder. The results indicate the potential of customized H_2^+ implantation techniques to enhance the properties of V_2O_5 thin films for advanced applications in optoelectronics and energy storage systems, facilitating further research in material science and engineering.

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