Synthesis & characterization of nanostructure VO\textsubscript{2} thin film

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Abstract Vanadium dioxides are strongly correlated systems which undergo an insulator-metal transition (IMT) from a low-temperature semiconducting phase to a high-temperature metallic phase. Among them, Vanadium dioxide (VO\textsubscript{2}) undergoes IMT close to room temperature, accompanied by a structural transition resulting change of several orders of magnitude in the electrical and optical properties. Here, we present the synthesis of VO\textsubscript{2} by sol-gel process which employs cost-effective precursors to synthesize pure phase of VO\textsubscript{2} thin films. The synthesized thin films were characterized using an X-ray diffraction (XRD) to confirm phase purity and high resolution scanning electron microscope (HR-SEM) to study the crystallite and particle size for the synthesized films. The film's surface was analyzed by X-ray photoelectron spectroscopy (XPS) to determine the valence state and chemical composition of vanadium dioxide.

Keywords. vanadium dioxide, sol-gel route, phase transition, silicon substrate

1. Introduction

VO\textsubscript{2} is an archetypal example of Mott insulator that manifests a reversible first-order insulator-metal transition (IMT) closer to room temperature (~ 341 K), which is a significant characteristic that drew substantial scientific and industrial attentions [1–6]. The VO\textsubscript{2} in its monoclinic (M1) phase at room temperature is a semiconductor; however, the rutile (R) phase of VO\textsubscript{2} is metallic across IMT [2–6]. Bulk and thin film VO\textsubscript{2} show a change in electrical resistance across the IMT by 1-5 orders of magnitude [3–6]. The IMT in VO\textsubscript{2} can be initiated by optical, thermal, electrical and mechanical stimuli [2–6]. Extensive investigations have been conducted to understand the microscopic origin of the insulator-metal transition in bulk VO\textsubscript{2}. However, the knowledge of such phase transitions at the nano length-scale with ultimate sensitivity to the orbital degrees of freedom is minimal and limited only to bulk or continuous thin films [7–12].

Different testimony methods have been utilized to manufacture VO\textsubscript{2} thin films, for example physical vapor deposition (PVD)/electron beam evaporation [13], sputter grows [14], chemical vapour deposition (CVD) [15] and pulse laser deposition (PLD) [16]. However, these deposition methods are large unpredictable and costly. Interestingly, the sol-gel synthesis method gives multiple benefits, such as deposition with large area, exact composition control, easy metallic doping and minimal cost [17–20] and also in this way, can be taken advantage of towards the advancement of enormous scope.
fabricating measures. Essentially, two sol-gel strategies are accustomed to fabricate VO$_2$ thin films. First includes the hydrolysis of vanadium alkoxides [21]. The surface morphology of the films prepared by this method shows well-crystalline faceted grains and minimal pinholes. Be that as it may, the antecedent used in this technique is exorbitant and sensitive to oxidation and water; along these lines requiring additional regard for keep all the apparatus perfect and dry during the whole interaction. Where as in the second method, liquid V$_2$O$_5$ is mixed into DI water to make V$_2$O$_5$ sol, which requires post-annealing at high vacuum to reduce V$_2$O$_5$ [22]. The films annealed at 823 K exhibit pure VO$_2$ phase with high crystalline nature. But this process requires a very high vacuum furnace. Also, maintaining such high vacuum at higher temperatures is difficult. A different and much simpler method, employing inexpensive precursors and equipments have been proposed [23–24], which uses vanadyl acetylacetonate as a starting material and 2-methoxyethanol as a solvent and involves simple heating in a controlled inert (Ar, N$_2$) atmospheric furnace to produce good quality thin films of VO$_2$ on Si substrates.

2. Experimental Part

2.1 Materials Synthesis
Sol-gel process was used to deposited the VO$_2$ thin films on silicone substrate with the help of spin coating system, utilizing commercially available analytically pure precursors Vanadyl acetylacetonate with chemical formula VO(acac)$_2$ (Sigma–Aldrich, 99%), 2-Methoxyethanol (99%) on p-type single-crystalline Si substrate. Vanadyl acetylacetonate was added into 2-methoxyethanol solvent. The precursor solution was continuously stirred by a magnetic stirrer for 24 h during the entire reaction. A transparent light red-greenish solution was obtained after the vanadyl acetylacetonate had dissolved totally. The precursor solution was aged for 15 to 20 days to achieve red-brownish colour at ambient temperature before spin coating.

2.2 Thin Film Deposition
The Si substrates were first cleaned through soap solution and rinsed through DI water. Thereafter, the substrates were cleaned by ultrasonically consequently with DI water, acetone and isopropanol for 30 minutes and doused with oxygen plasma for 10 min (25 W) before spin coating to eliminate the leftover natural substance and to make them hydrophilic. The solution was coated on hydrophilic clean Si substrates at 3500 rpm for 50 seconds and dried on a hotplate at 363 K for 20-30 minutes to eliminate exorbitant water and organics. Finally, the pre-deposited films were annealed at 823 K for 45 minutes in the presence of an argon atmosphere (Purity > 99.99%) with the heating rate of 10 °C/min. After natural cooling, the resultant high crystalline pure VO$_2$ thin films obtained.

3. Results and Discussion

3.1 Phase characterization
The crystal structure of VO$_2$ thin films were checked by X-ray diffraction (Rigaku Miniflex BT-XRD machine) with Cu-K$_\alpha$ ($\lambda$ = 1.5418Å) radiation source. The output rate was kept at 3 degree/minute for 20° to 60° sweeps with the progression size of 0.02°. Thin film XRD spectra of VO$_2$ display in Fig. 1. A major peak was observed at $2\theta$ = 27.34°, with full-width half-maximum of $w_{1/2} = 0.34°$, attributed to the monoclinic phase of VO$_2$ with the orientation (011). It is worth noting that the peak position slightly shifted compares to the theoretical value (27.87°). This shift can be understood as a result of lattice mismatch between the VO$_2$ thin films and the Si substrates, this also leads to a different value for interplanar distance $d = 3.25$ Å. The Bragg’s peak 27.34° represents the M1 phase of VO$_2$ in the (011) orientation. The average crystallites size (D) was determined by utilizing the Scherrer formula.

$$D = \frac{0.94\lambda}{(w \times \cos \theta)}$$

(1)
Where \( w \) is full-width half-maximum (FWHM) of the Bragg’s peak, that is estimated by interpolation of Bragg’s peak at \( 2\theta = 27.34^\circ \) using a pseudo-Voigt function, \( \lambda \) is the wavelength Cu-K\( \alpha \) (1.5406 Å), and \( \theta \) is the Bragg’s angle corresponding to the peak (011) of VO\(_2\). The value of \( D = 24.82 \) nm is estimated for the sample.

Figure 1. Thin film XRD-spectra of VO\(_2\) annealed at 823 K and inset shows the highlighted part of (011) Bragg’s peak along with its pseudo-Voigt function fit.

3.2 Surface morphology
The morphology of nanostructure VO\(_2\) surface was seen by a Field Emission Scanning Electron Microscope (FESEM) FEI Nova NanoSEM 450. The films exhibit round uniform nanocrystalline grains, which exhibit low porosity/pinholes among grains and appear such a compact homogeneous surface as shown in Fig. 2. The particle size favours the average crystallites size (D) calculated from XRD, which is a very good agreement.

Figure 2. FESEM images showing the surface morphology of the VO\(_2\) thin films annealed at 823 K.
3.3 Valence state of vanadium
To determine valence state and chemical composition, VO$_2$ thin film was analyzed by XPS (K-Alpha, Thermo Fisher Scientific). The comparing study output and center level spectra of V$_{2p}$ of the films are given in Fig. 3. The XPS spectra were changed with the C$_{1s}$ peak (284.5 eV) from the CO$_2$ held on the film surface or with the debasement from the conductive carbon tape used to tie the petite film. The V-O bond, O$_2$, CO$_2$ or H$_2$O can offer to the wide O$_{1s}$ peak at around 530.2 eV. The peak for Si$_{2p}$ is credited to the substrate and may be a result from the lower film thickness. The center level spectrum of V$_{2p}$ shows two typical peaks (V$_{2p3/2}$ and V$_{2p1/2}$) in Fig. 3 (b) due to the orbital splitting. The V$_{2p3/2}$ pinnacle is more fragile to different vanadium valences. The vanadium valences were determined by fitting the pinnacle position of V$_{2p}$ with XPS top fit programming, as displayed in Fig. 3 (b). In Fig. 3 (b), the center level spectra of V$_{2p}$ shows one valence condition of vanadium, +4 valence (with an energy of 515.8–516.6 eV), which implies that the principle valence condition of vanadium is +4.

![XPS spectra](image)

**Figure 3.** XPS spectra (a) XPS survey scans (b) Fitted center-level XPS spectra of VO$_2$ thin film annealed at 823 K.

4. Conclusion

We have successfully grown the nanostructure VO$_2$ thin films on Si substrates through sol-gel/solution route. The fundamental change in our technique was to utilize 2-methoxyethanol as a solvent to control the fabrication of isolated grains and achieve a compact surface morphology. The oxidation states of V indicate the formation of VO$_2$ thin film in its pure phase.

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6. References

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