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Investigation of preparation method on vanadium oxide thin films thermochromic tendency under high annealing temperature

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Abstract : The effect of investigation method on the vanadium oxide thin film transition temperature have been investigated. Three coating solutions were adopted; first starting from vanadium (V) oxytripropoxide precursors mixed with anhydrous isopropanol with and without tungsten chloride. While the other two solution starts from vanadium metal or vanadium pentoxidemixed with hydrogen peroxide. Spin coating technique was used to prepare the tested films,at spinning speed of 2800 rpm, using (1×1 cm) quartz substrate. The effect of annealing temperature on the films structure were investigated too. The resulting films were characterized through UV-VIS-NIR, SEM, XRD and FTIR. The doping concentration effect on films thermochromic properties was investigated.

Introduction

Smart windows, defined as the kind of windows that partially prevent the unwanted solar radiation. This property can enhanced by increasing heat gain in wintry weather and decreasing it in warm weather by adopting glasses irradiative and thermal features dynamically [1]. Coating convenient absorbing layer on the surface of the glass can modify the optical properties of this glass by regulating the fallen solar heat flux [2]. Thus smart windows lead to reduced heating freshening and air conditioning energy consumption, size and electric request of the building [3,4].Smart glasses latest equipment, include thermochromic, electrochromic, photochromic, micro-blind and polymerisolated liquid crystal devices[5].

F. J. Morin in 1959 was firstly discovery of the VO_2 transition [6]. At low temperature, VO_2 has a monoclinic crystal structure. If VO_2 films was heated over the transition temperature (around 68°C), the lattice is changed from the monoclinic to a tetragonal crystal phase, then enabling the material to be IR reflecting.

Practically, in addition to VO_2, there are corresponding vanadium oxides often resulting from preparation methods, which are commonly known as Magnelli phases V_nO_{2n-1} [7].The mainvanadium oxide phases are V_2O_5,VO, VO_2 and V_2O_3, which reveal different oxidation states V^{2+},V^{4+}, V^{3+} and (V^{5+}) respectively.

Usually, vanadium dioxide thin films are synthesized through physical vapor deposition, chemical vapor deposition and sol-gel method. Sol-gel method is starting from; precursor solution, its transformation into sol and then into gel due to hydrolysis and condensation processes, following by aging, drying and thermal treatment. In fact fabrication of thin films can occur on the gel stage, where the obvious advantage of sol-gel method is the high degree of initial components homogeneity.

Researchers have to pay particular attention to the direct dependence between the synthesis methods and conditions and products physical properties. Furthermore, the film morphology also greatly influences the phase transition characteristics, mainly on the thermal hysteresis loop width. The effect of synthesis conditions on the reaction products is also evident for sol-gel approach [8-10]. Sol-gel technology can also be used to synthesize doped VO_2 thin films on fluoride tin oxide [11], aluminum [12], silicon [10], titanium oxide [13], Laminate Films [14]or glass [15] substrates. Furthermore, vanadium pentoxide reduction on the substrate [16, 17] is one of the possible modifications of VO_2 sol-gel synthesis, the initial Magnelli phases can be converted into VO_2(B) and VO_2(M) [17].

Morphology together with particle size and doping are the main parameter that determines the VO_2 properties. The various existing ways for VO_2 synthesis are quite assort and numerous variations of composition, dimension distributions and material structure can be achieved. This raises new ambitious areas for the scientists. The improvement of known synthetic techniques as well as the development of novel synthesis approaches are very perspective in order to discover modern products with more complicated structures and compositions.

The aim of this investigation is fabrication of vanadium oxide W-VO_2as thermochromic composite films using the VO_2 orW-VO_2 coating. Also studying three preparation methods of vanadium oxides thin film, then examine the tungsten chloride doping concentration affection on the transition temperature.

2. Experimental

2.1. Material

The chemicals used for the preparation of vanadium oxide films were

Table (1) materials that used in this study.

Material	Equip with	purity
Vanadium oxytripropoxide	Sigma-Aldrich	98%
Metallic vanadium powder	Sigma-Aldrich	99.7%
Vanadium pentoxide	Sigma-Aldrich	≥99.6%
Tungsten hexa-chloride	Sigma-Aldrich	≥99.99%
Hydrogen peroxide	Chemistry lab	97%
Anhydrous isopropyl alcohol	Chemistry lab	≥98%
Glacial acetic acid	Chemistry lab	≥99.5%
Calcium oxide	Chemistry lab	98%
Ethanol alcohol	Chemistry lab	99%

2.2. Procedure

In order to prepare vanadium oxide films, three procedures were adopted;

First procedure, briefly; starting solutionsfor produce vanadium oxides thin films were prepared by mixing vanadium oxytripropoxide in an anhydrous isopropyl alcohol as solvent with and without glacial acetic acid. This mixture was stirred for 30 min at room temperature. The films were deposited by spincoating method(2500 rpm for 1min). These films were subsequently dried in air at room temperature for 30 min, and

next thermal treated at 800 ^{0}C for 60 min. For preparing tungsten doped vanadium oxide, three concentrations of tungsten chloride (1, 2 and 4 wt.%) were add during the sol phase. The sol turned bright yellow upon adding WCl_6after 30 min of stirring the solution color was shifted from yellow to blue. This is said to occur because W^{6+}(yellow) is reduced to W^{5+} (blue) by the organic solvent.

Second Procedure, briefly; V_2O_5 powder 0.51g was slowly dissolved in hydrogen peroxide solution 50 mL30% under stirring at room temperature until clear orange solution formed. After stirring for another 15 min and aging for 2 days at room temperature, the solution gradually turned into a dark red V_2O_5 gel. The resulting gel was transferred into a funnel and washed with ethanol five times, then immersed in ethanol for 7 days and a jelly-like precursor finally formed.

Third Procedure, briefly; metallic vanadium powder 0.3 g was dissolved in 30% hydrogen peroxide solution 30 mL in an ice bath with rigorous stirring for 40 min. The clear yellow solution was then heated at 50 °C with continuous stirring until the color of the solution changed from yellow to dark red and then returned to yellow. Prior to usage, the gel shouldbe aged at room temperature until uniform dark red gel is formed.

2.3. Characterization

UV-Visible and IR spectra were recorded in the range of (300 – 1000) nm and till 2500 nm, using double beam (JASCO V-530) UV-Visible spectrophotometer and PerkinElmer UV WinLab 6.0.3.0730 / 1.61.00 Lambda 900respectively.The crystal structures were tested using XRD instrument from [(STOE) Company/ Germany, model, STADI/MP], operated at (40kV) and (30mA), which isused (CuKα) radiation source at wavelength (λ) of (1.54Aº). The microstructure and morphology of films were observed by field emission scanning electron microscopy FESEM("Hitachi", model/S41-60).

Results

All vanadium films were coated on quartz substrate and annealed at 800 ˚C, otherwise will mentioned in each case.

Optical investigation

Since, sol gel method producing more homogeneous films, as expected there samples reveals the highest transmittance, while the film prepared starting from vanadium pentoxide powder present the lowest transmittance. The difference between the two powder samples transmittance may be reflect the lower oxide reaction activity with hydrogen peroxide than that of metal, resulting in difference in their solution homogeneity. Transmission spectra in the visible region for the vanadium oxides films prepared starting from VTOP without and with acidic acid, vanadium metal powder and vanadium pentoxide powder are illustrated in figure (1-a).

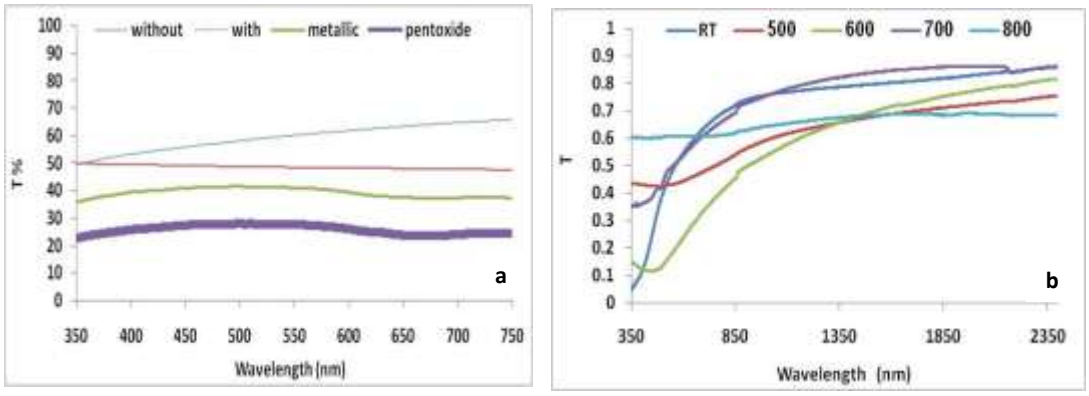

Figure (1) Transmission spectra for vanadium oxides films prepared adopting different recipes.

The variation in transmittance with annealing temperature may be attributed to the deferent crystal sites and sizes at each of these temperatures. It is noticed that if samples annealed at 800˚C, the annealing process was enhanced the optical transmittance in the visible region figure (1-b). As for thermochromic glass application it is important region for visible light entrance throw windows. Therefore the sample annealed at 800 ˚C may represent the favorite choice in this matter.

SEM investigation

As mentioned earlier, the temperature at which the tested samples were annealed was 800 ˚C. The image disclosed that at this high temperature, the vanadium pentoxide sample film was condensing into very large particles (about 0.5-2.0 μm).Though, instead of forming a mass of adjoining crystals, this sample resulted in large, isolated crystals.

The SEM images for the vanadium film that prepared by vanadium metal was illustrated in figure (2). The crystal structures manifested as uniform striped cones. Several separated nanoparticles are associated with the large particles according the crystal site and on the top of the crystal surface. The SEM images of these particles are mentioned by yellow dotted arrow as shown in figure (2-a), also this image show two phases separation clearly and the variation in size of these cones are presented in figure (2-b). Theses crystals were well distributed through the sample as shown in figure (2-c).

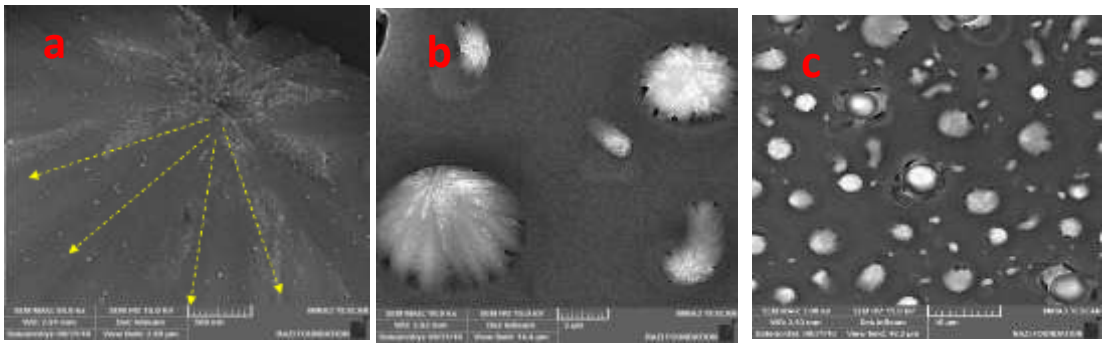

Figure (2) SEM images for the vanadium oxide film prepared from vanadium metal

Generally, the images of vanadium pentoxide film reflect shielded packages containing several aggregated sphere liked nanoparticles in each package. Regarding to the shape of these nanoparticles, it may be related to the unreacted original vanadium pentoxide. The average particle size of the non-aggregated nanoparticles was about 20 nm. The shielded packages may manifested themselves three or more packages connected together, producing jointed larger sites figure (3-7a). The crystal structures in this case were marked fairly uniform striped cones affected by the shielding field, which may limited their identical growth. The particles size of these sites was about (2 μm) and it has somewhat a narrow particle size distribution figure (3b).

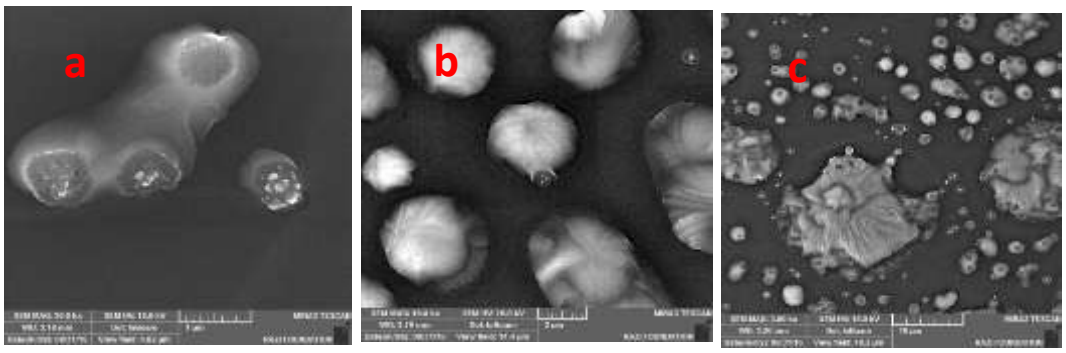

Figure (3) SEM images for the vanadium oxide film prepared from vanadium pentoxide

Figure (3-c) bring to light the initiating of few separated and relatively large flower like crystal sites of (10 μm) in size, which imitate the formation of another crystal structure together the previous one. May be these crystal have a good chance for creating from well dissolve vanadium pentoxide powder in hydrogen peroxide.

The images of the film prepared by starting from VOTP with acidic acid recipe was seemed to be like that of vanadium film that prepared by vanadium metal, figure (2). However, the striped cones were also exist but they were not of the same uniform as the vanadium metal sample figure (4-a), in fact there were small variations. Where the nanoparticles which were on the top of the crystal surface did not associated with the large particles according the crystal site figure (4-b). Although, the crystal sites, here, have narrower particle size distribution figure (4-c).

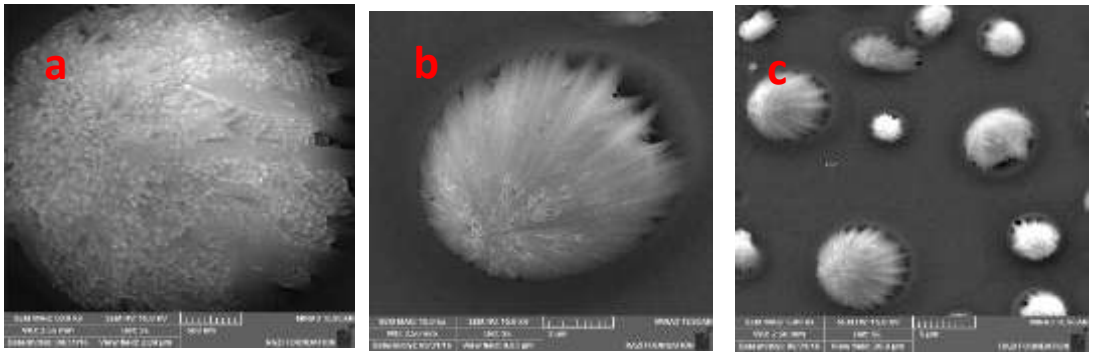

Figure (4) SEM images for the vanadium oxide film prepared VOTP with acetic acid

Figure (5) present the SEM images for the vanadium film, which was prepared by starting from VOTP without acidic acid recipe. The film image at a high magnification, 200kx, reflect homogeneous structure of particle size of about (10 nm) and of narrow particles size distribution figure (5-a). While, as the magnification was reduced to 30kx the film show clingy flower like structure indicating to the present of somewhat crystal sites figure (5-b). Further reduction in magnification displays multilayer crystaline structure. The structure seem to be reducing it self layer by layer forming accumilated short pyramid shapes figure (5-c).

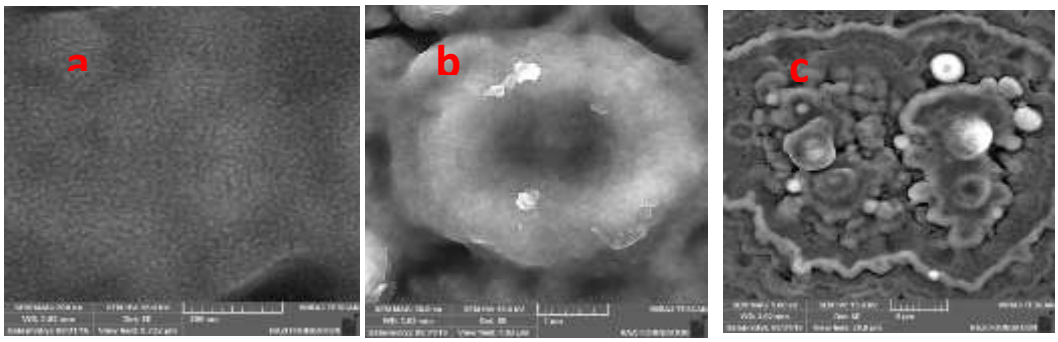

Figure (5) SEM images for the vanadium oxide film prepared VOTP without acetic acid

The bright circules on the image may be due to the variation in high of the formed pyramid shapes. May be the non sufficient annealing time, just one hour, was leading to not totally crystal formation, which clear being in the variation of crystal sites sizes.

Figure (6) present the SEM images for the tungsten chloride doped vanadium film at doping concentration of 4 w%, which was prepared by starting from VOTP without acidic acid recipe. This film displayed, at the first look, different crystal sites, figure (6-a), which were expected as tungsten chloride was take on here. The nanoparticles dispraised on the striped cones may make use of tungsten ions to enhancing their growth producing well definite tree leafs like crystal sites figure (6-b). These well build crystal sites were dominated on the film surface and may destroyed the previous striped cones sites.

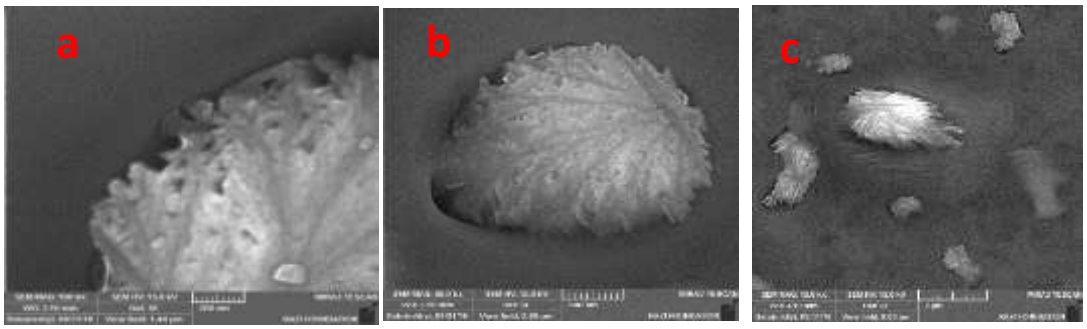

Figure (6) SEM images for the tungsten chloride doped vanadium oxide film

We have not observed a uniform particle size in any of these samples, nor should we expect to. Where, several crystal sites were presented in the film under low magnification image, figure (6-c). These crystal sites may reflect the creation of number of oxides of vanadium and tungsten.

XRD investigations

Figure (7-a) present the XRD spectra for vanadium oxide films prepared at different recipes. Both powder recipes spectra show more than single crystal phase and the peaks were roughly broad indicating to their nanostructure. However, vanadium pentoxide film spectrum records several peaks which confirm the results presented by SEM figure(3). The VO_2 crystal phase didn't recorded in metallic recipe film, while vanadium pentoxide film spectrum records low intensity peaks related to this crystal phase. In without acetic acid recipe spectrum, the peak located at 2Θ (40.91) may be related to V_2O_3 according to (26-278) and 2Θ (21.50, 47.55) may be related to V_2O_5 according to (9-0387) while the broad peak located at 2Θ (35.5) may be related to VO_2 according to (31-1439).Whereas, in the case of with acetic acid recipe film, only one peak was clearly recorded in the spectrum of this film, this peak was located at 2Θ (21.89) and it may be related to V_2O_5 according to (9-0387).

Figure (7-b) show strong peak at 2Θ (21.4) which may be related to V_2O_5 according to (9-0387) while the peak located at 2Θ (31.3, 35.6, 55.4, 56.8) may be related to VO_2 according to (42-0876).

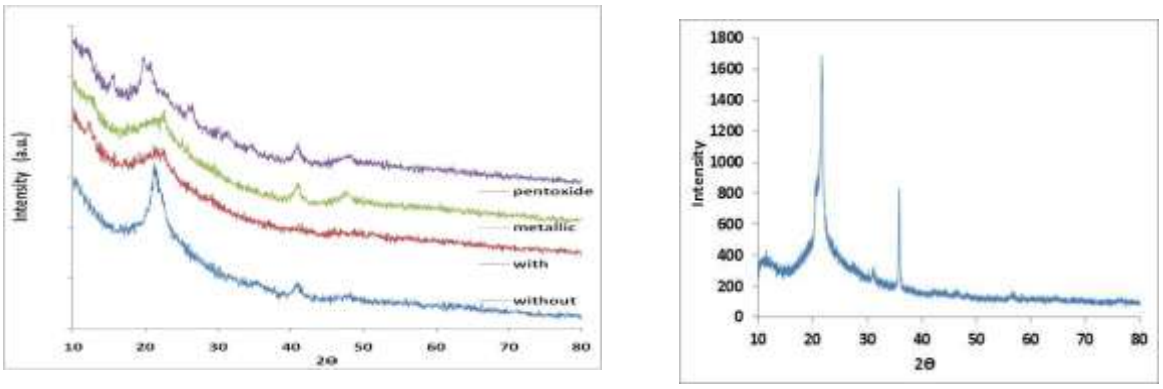

Figure7. XRD spectra for films prepared (a) at different recipes, (b) doped 4% tungsten chloride

Thermochromic investigation

In order to determine the thermochromic transition switching temperature, the films transmittance at 1300 nm was measured at the same time as the temperature was cycled during the metal-to-semiconductor transition.

In all three doped films, the hysteresis width was found to be between 9 and 13 ºC. Perfectly this would be as small as possible to maximize the power benefit of including this type of thermochromic films. However, the thermochromic transition temperature decreased to as low as 49 ºC for a VOTP thin film doped with 1 % tungsten with hysteresis loop width about 9 ºC. As the amount of tungsten in the films increased the hysteresis width was also found to increase reaching 11 ºC and 13 ºC with thermochromic transition temperature decreased to 52 ºC and 49.5 ºC for films doped at 2 % and 4% respectively, figure (7).

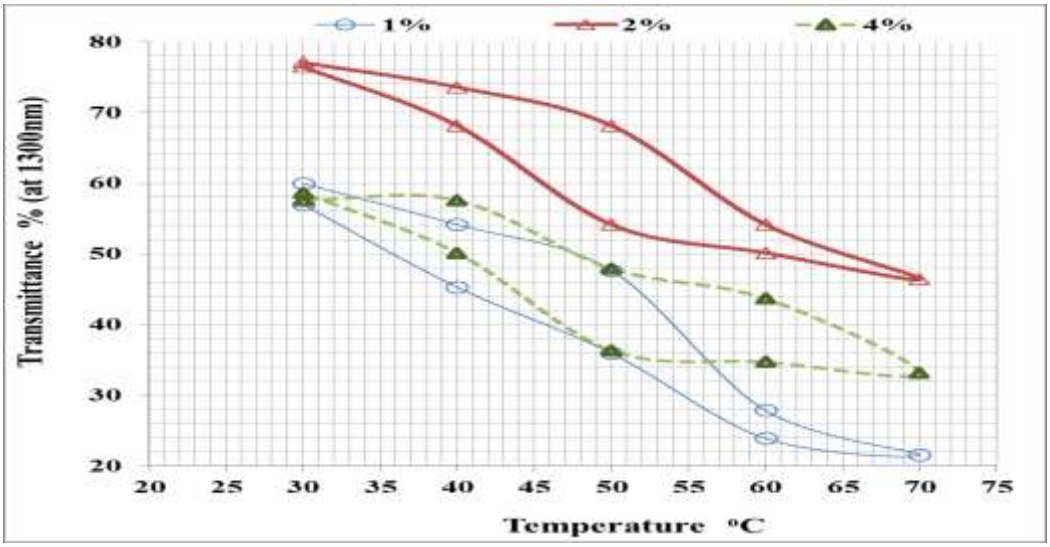

Figure (8) Hysteresis loops width and average transition temperature for tungsten chloride doped VOTP films without acetic acid at doping concentration of (a) 1% (b) 2% and (c) 4%

It can be seen that for the W-doped films there is a net decrease in the Tc value; besides, the width of the hysteresis loop is fair, making the material even more suitable for an intelligent material coating.

Perhaps this variation may be due to a larger number of defects in VO_2 lattice which would cause a bigger variation in the temperatures as a result of which different regions of the film would go through the transition.

Conclusion.

Vanadium dioxide thin films were successfully synthesized under optimized condition on quartz substrates through; vanadium metal, vanadium pentoxide and VOTP low temperature sol gel method. Maybe the most important result of this study is the reduction of tungsten doped vanadium oxide transition temperature from 68 ºC to about 49 ºC, which is commonly recorded in hot countries outside the building specially in July and August. The study revealed that the increase in annealing temperature to 800 ºC can well arrange the grains alignment in the films. Also the random alignment of the grains in microstructure of the film leads to the decrease in optical properties of the film. The optical properties demonstrate dependence in the nanostructure of the films.The adopted techniques must be in a high-quality working condition in order to obtain good outcomes.

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