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Carbon Nanotubes Doped Vanadium Oxide Thin Film

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Vanadium oxide films were prepared by chemical coating techniques on glass and ITO coated glass substrates. Vanadium oxide films were doped with carbon nanotubes and examined their optical band gap and structures. The effects of carbon nanotubes on visible light absorbance and band gap energies were observed. Electrochemical, structural and optical studies on vanadium oxide coatings were reported in the liquid electrolyte. Optical constant such as refractive index, extinction coefficient, and band gap calculation was done by NKD analyzer. Effect of CNT into vanadium oxide films structural properties were examined by atomic force microscopy (AFM)

Keywords: CNT, Vanadium Oxide, Thin Films, Sol-Gel, Electrochromism.

PACS numbers: 61.46.Fg, 68.55. – a

1. INTRODUCTION

Vanadium oxide are widely used in optical and electronic applications. These applications can be classified as thermochromic coatings for windows, high-speed optical and electronic switches, catalytic, electronic information displays, color memory devices, solar energy panels for small, high-capacity Li-ion batteries and thermal sensors as exemplified coatings for the cathode. CNT-VO_2 composite systems are presently not being taken for these applications including their potential use to address environmental problems. VO_2 is one of the best candidate materials due to high-speed optical and electronic switches properties, and long-term thermodynamic stability. CNT-VO2 composite system is expected to improve the optical and electrical properties.

In this study, it was tried to develop the activation region of vanadium by doping it with CNTs. CNTs have excellent electronic properties, large surface areas and also allow for chemical bonding modifications.

In realizing the experiment, two different solutions were prepared: only vanadium oxide solution as the control group and CNT-vanadium oxide solution as the experiment group. Corning glass and ITO glass substrates were coated in metal alkoxide precursors by a dip coater. After that, they were undergone some heat treatment. Finally, the samples were characterized via NKD analyzer, AFM and CV.

Vanadium oxide films and CNT doped vanadium oxide films were prepared and characterized separately. Vanadium oxide and carbon nanotubes doped vanadium oxide films were heated at 100oC. Optical and structural characterization of as-deposited and heat treated films were investigated and compared with each other.

2. EXPERIMENTAL PART

2.1 Preparation of Films

The substrates were cleaned distilled water, acetone, methanol and ethanol in turn. The vanadium oxide sol, was prepared by dissolving vanadium oxytriisopropoxide (2 ml) in isopropanol solution (60 ml) with stirring for 1 h. A small amount of nitric acid was added to the solution as catalyst. Other solutions including a desired amount of CNTs (2 ,4, 5 and 6wt% of the produced VO_2 in the sol) were also prepared. The CNTs were multi–walled carbon nanotube (MWNT) powders of >95% purity with outer diameter of 20–30 nm and length of 10–30 um. For aging the solution, it was left for 24 hours at the room temperature. The CNT–doped VO_2 films were deposited on Corning and ITO glass substrates by a dip-coating method. The substrate immersed in the solution for about 1 minute was pulled at constant speed of 1 mm.s^{-1} by using the dip coater. After drying the samples at room temperature for 24 hours, they were heat-treated at 100^{o}C in air for 1 hour. Undoped VO_2 thin films were also synthesized by using the same procedure.

3. RESULT AND DISCUSSION

NKD analyzer with reflection and transmittance in the wavelength range 300-1000 nm measured.

Looking at all the curves in Figure 1 in general, the CNT doped films T value is shifting to longer wavelengths in UV region . CNT films with the contribution of this behavior show a decrease in band gap as shown in Table 1 and Figure 2. Especially transmittance values of 2%CNT doped VO_2 films shift to longer wavelength. T values decrease along the whole spectrum of the CNT doped films (Figure 1). Refractive index curves of the NKD extinction coefficients were calculated using the software program how to change the values of n and k of films.

Table 1 – Band gap values of the films

Samples	Band Gap (eV)
0	2.52
2%	2.48
4%	2.49
5%	2.50
6%	2.51

Atomic force microscopy (AFM) was used to study the structure of the all deposited layers in Fig. 3. The images indicate that VO_2 films with amorphous structure,

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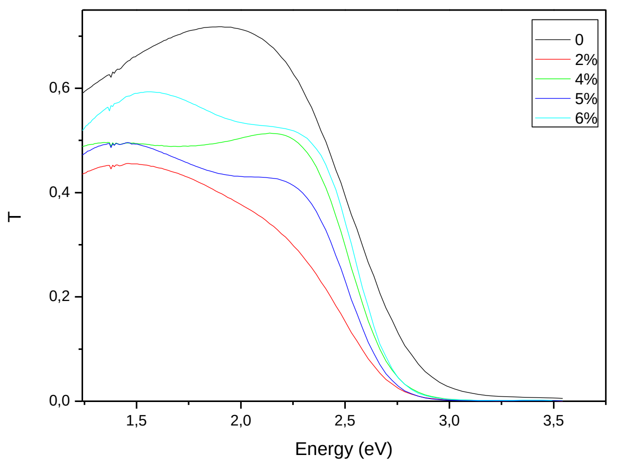

Fig. 1 – Transmittance versus energy curves of all deposited films

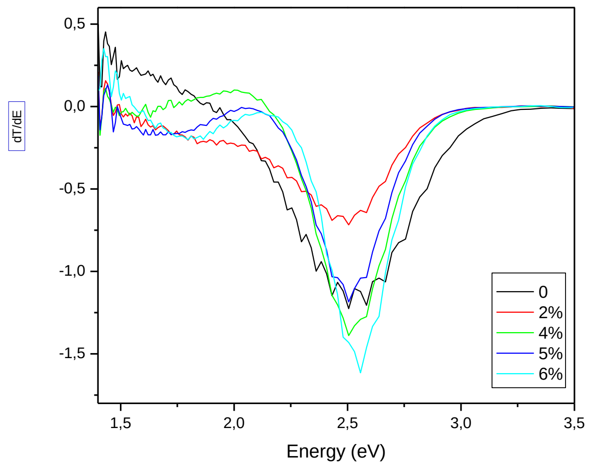

Fig. 2 – dT/dE curves of all deposited films

which has very regular structures include multi-walled CNT structure ensures to become more regular. VO_2 films coated with sol-gel method, as expected, has a porous structure. Caused a decrease in the pore structure of the contribution of CNT films and structures has become more rigorous and regular. This result is consistent with the T-λ curves. Significant decreases in T levels was observed with the contribution of the CNT. The all as-deposited films were then exposed to electrochemical and electrochromic investigations using $LiClO_4$ in propylene carbonate as an electrolyte. The CV of vanadium oxide films are given in Fig. 4-8. The results demonstrated that the CNT cause change on the electrochemical and structural properties of vanadium oxide films. Vanadium oxide film coated on the ITO electrode carrier of the study, the platinum plate was used as the counter electrode. 1 M LiClO4/PC used as the electrolyte. With an applied voltage range between -1 V and 10mV / s to 100 mV / s was done at different scan rates. Vanadium oxide becomes transparent while the negative current values applied, and positive current values that the brown-colored state. All coloring is reversible, the increase in scanning rate. Differences have been observed CV behavior of CNT doped films. Especially as the amount of CNT has been an increase in CV. CNT films doped with 4-6% CV behavior is similar to the behavior of super-capacitors. It will be studied in more detail in CV curves. This interesting observation may be related to porous structure of these films. This result should be examined in term of super capacitive properties of these films in the further work.

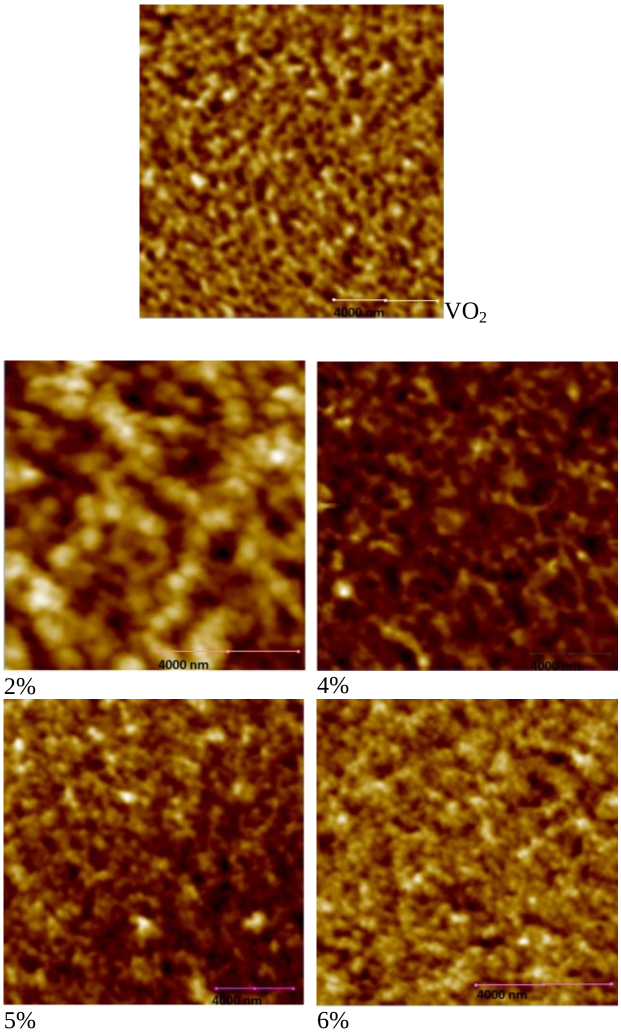

Fig. 3 – AFM imaged of the films

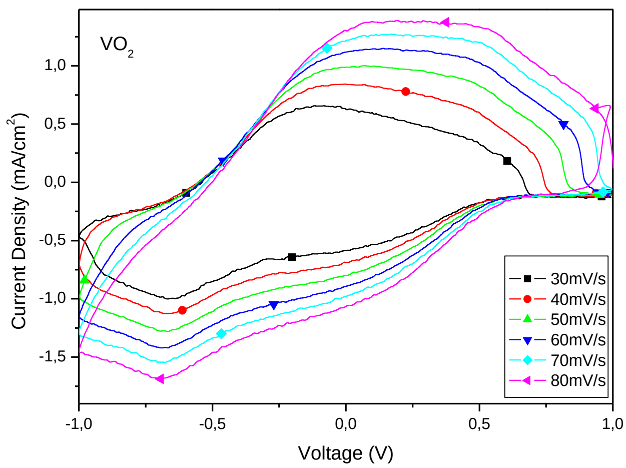

Fig. 4 – CV curves of vanadium oxide films with various scan rates

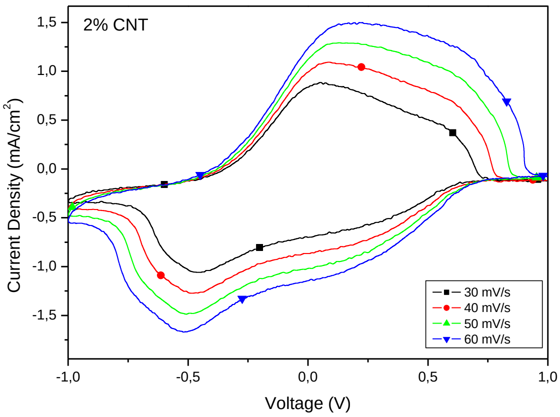

Fig. 5 – CV curves of 2% CNT doped vanadium oxide films with various scan rates

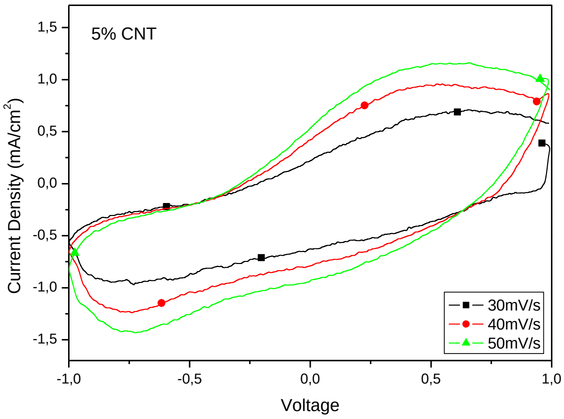

Fig. 7 – CV curves of 5% CNT doped vanadium oxide films with various scan rates

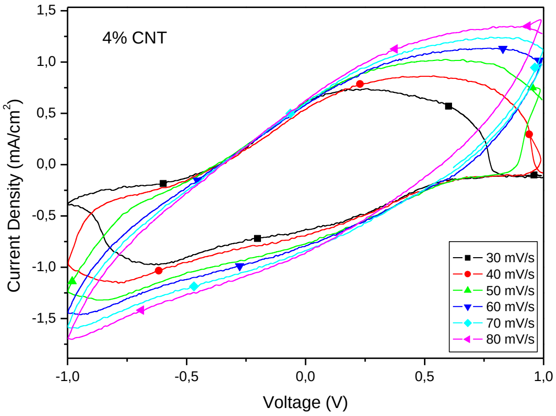

Fig. 6 – CV curves of 4% CNT doped vanadium oxide films with various scan rates

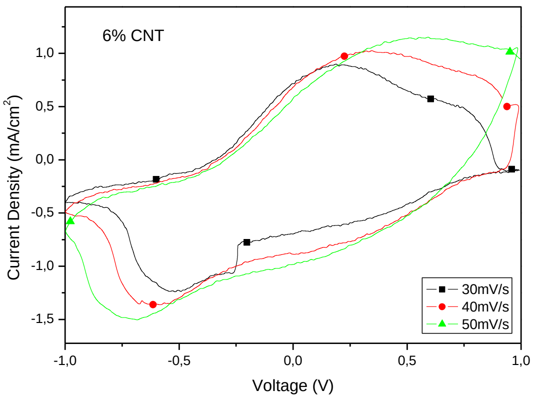

Fig. 8 – CV curves of 6% CNT doped vanadium oxide films with various scan rates

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