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First synthesis of vanadium dioxide by ultrasonic nebula-spray pyrolysis

Bonex Wakufwa Mwakikunga [a,*], Elias Sideras-Haddad [a], Malik Maaza [b]

[a] *School of Physics, University of the Witwatersrand, Private Bag X3, P.O. Wits, Johannesburg, Gauteng 2050, South Africa*
[b] *iThemba Labs, P.O. Box 722, Somerset West 7129, Cape Town, South Africa*

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Abstract

Vanadium dioxide synthesis is a special problem from any precursor material due to the multi-valence nature of vanadium oxides and the fact that, among these oxides, VO_2 is one of the most unstable of them. Its synthesis therefore must be done under properly controlled conditions. This paper reports on the results of the production of the sub-micrometer structured VO_2 thin films for the first time by the ultrasonic nebula-spray pyrolysis from the precursor vanadium tri-chloride in an aqueous solution of 0.085 M ammonium meta-vanadate. The optimized flow rate of the argon carrier gas was 11 ml min^{-1} and VO_2 was obtained at deposition temperature well above 600 °C. Infrared switching confirms the VO_2 transition temperature in the neighborhood of 60 °C for samples prepared under argon whereas, those prepared under oxygen show a drastic shift in transition temperature to the neighborhood of room temperature (23 °C).

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1. Introduction

Thermo-chromic materials are characterized by a semiconductor-to-metal transition occurring from a reversible change in their crystalline structure as a function of the temperature. Along with a change in optical properties are also electronic transitions evidenced by a change in electrical resistivity. This change has been observed in transition-metal oxides [1,2] such as Ti_2O_3, Fe_3O_4, and Mo_9O_{26} and in several magneli phases of vanadium oxide, V_nO_{2n-1}. Among them, VO_2 has received the most attention because of the large reversible change of electric, magnetic and optical properties at temperatures around 70°C [3].

During the semiconductor-to-metal transition, the optical properties of vanadium dioxide are characterized by a sharp decrease in optical transmission in the infrared spectrum. This is coupled with an increase in its reflectivity. Because of this anomalous behaviour, vanadium dioxide has been presented as an attractive thin film material for electrical or optical switches, optical storage, laser protection, and solar energy control for windows in space satellites.

The transition temperature of vanadium dioxide of 70 °C may be decreased by the addition of high-valent transition metals such as niobium, molybdenum or tungsten. Trivalent cations (chromium and aluminium) increase the transition temperature. The hysteresis profile associated with the transition depends on the microstructure and crystallinity of the sample.

Since the discovery of the VO_2 semiconductor to metal transition by Morin in 1959 [3] VO_2 has been a subject of numerous experimental and theoretical studies. In the first-order [3] phase transition of VO_2, the material undergoes a reversible change from a tetragonal rutile structure phase, space group *P4₂/mnm* with typical lattice constants $a = 4.5546$ Å and $c = 2.8514$ Å, at higher temperature to a monoclinic structure, space group *C2/m* with lattice constants $a = 12.09$ Å, $b = 3.702$Å, 6.433 Å and $\beta = 106.6°$,

* Corresponding author.
E-mail address: bonex_mwakikunga@yahoo.com (B.W. Mwakikunga).

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below the phase transition temperature [4]. These structural characteristics led Goodenough [5] to propose a model of the electronic structure based on the molecular field theory that has accounted for some properties of VO_2 metallic and semiconducting phases [6]. This model has subsequently undergone further improvements by incorporating electron–electron correlations [7] and electron–phonon interactions.

Because of the ability to change the transition temperature by doping, Lee et al. [8] and more recently Jin et al. [9], suggested that tungsten doped vanadium dioxide can be used in energy efficient windows. These smart windows or electro-chromic displays find special applications in the architectural, automotive and aerospace sectors [11]. Roach [11] pointed out that, due to the changes in reflectivity during the phase transition, VO_2 films can be used as a kind of optical disc medium and demonstrate holographic storage. Bit recording on VO_2 films using a near-infra-red laser was demonstrated [12]; stability during long-term storage and over 10^8 time cycles of write and erase were achieved without degradation. Switching time of about 30 ns and writing energy of the order of a few mJ/cm^2 were reported [13]. Bit density has been estimated to be 350 bits/mm. Such low threshold recording energy and erase-rewrite abilities encourage the use of VO_2 films as a recording medium [14]. More recently, the use of VO_2 thin films was suggested in ultra-fast optical switching devices. The high-temperature metallic state attained in 5 ps by using femto-second laser excitation at 780 nm was reported [15]. In summary, vanadium dioxide is an interesting candidate for modern applications of active thin films in optical or electric [16] switches.

VO_2 has been prepared by vapour transport method [17], ion implantation [18], hydrothermal technique [19] for nano-wires and nano-belts; r.f. sputtering [20,21], sol gel technique [22] and pulsed laser deposition [23] for thin films. In this article, synthesis for the first time of micro-structured thin films of VO_2 by ultrasonic spray pyrolysis process is reported. The only work that precedes this work was on V_2O_5 by spray pyrolysis by Bouzidi et al. [24]. V_2O_5 is the most stable of vanadium oxides and this is the initial candidate that is present in most synthesis processing. To obtain VO_2, one of the most unstable oxides, controlled conditions are required. The present article reports on the work geared to obtaining VO_2 with optimized conditions in ultrasonic spray pyrolysis process.

2. Experimental

A precursor solution of ammonium meta-vanadate mixed with vanadium tri-chloride, $NH_4VO_3 + VCl_3$ (coded AMVC) was prepared. The AMV was a whitish yellowish powder with molecular weight of 116.98, density of 2.326 g cm^{-3} and a melting temperature of 200 °C. Surface tension of the precursor solution was measured using the capillary rise method. A scoop weighing 6.1 g of AMV and was dissolved in 600 ml of distilled water and mixed well using a magnetic stirrer on a hot plate at around 70 °C for about 3 h. The so-made solution was then decanted into the container that was housing the ultrasonic nebulizer operating at a frequency of 1.7 MHz as illustrated in the schematic diagram of Fig. 1. Substrate mate-

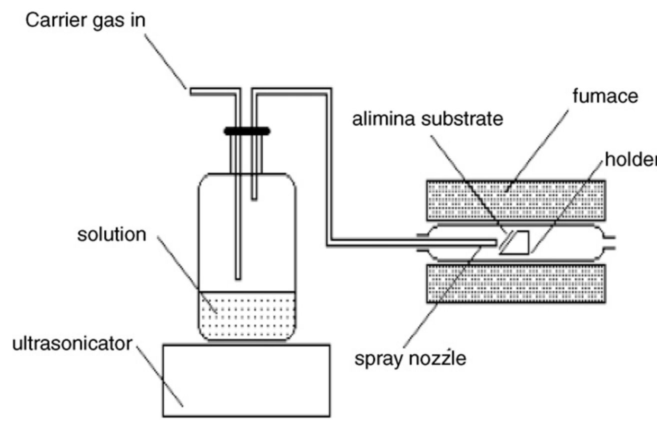

Fig. 1. A diagrammatic layout of a typical set-up of the ultrasonic nebula-spray pyrolysis technique.

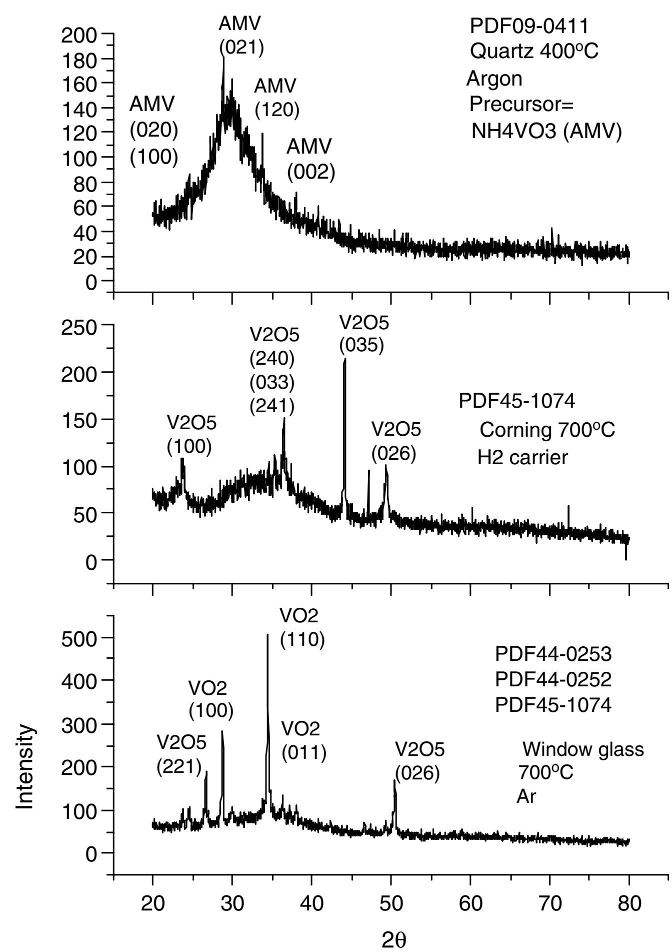

Fig. 2. Typical X-ray spectra of VO_2 under different synthesis conditions-carries gas type, carrier gas flow rate, substrate type, substrate temperature.