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# Enhanced infrared sensing properties of vanadium pentoxide nanofibers for bolometer application

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ABSTRACT

The main aim of this work is to report an alternative technique of creating vanadium pentoxide ($V_2O_5$) based uncooled infrared (IR) detector, by a state-of-the-art $V_2O_5$ nanofibers, manufactured by facile and economical electrospinning process. The nanofibers were thermally and electrically characterized to determine their bolometric performance. The nanofibers show maximum voltage responsivity ($R_v$) 6987.3 V/W at 100 mA DC bias, in a normal room temperature and pressure condition. Nanofibers show very good thermal response ($\tau_s$) and recovery time ($\tau_r$) when subjected to a periodic On-Off cycle of IR lamp (150 W) illumination. Temperature dependent resistance measurement shows that nanofibers are exhibiting semiconductor to metallic phase transition at 67 °C with maximum temperature coefficient of resistance (TCR%) − 1.6%/K at the transition. $V_2O_5$ nanofibers characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman Spectroscopy confirms their crystallinity and elemental composition. The optical band gap of the nanofibers is analyzed by UV–Visible spectroscopy. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images confirms their microstructural dimensions and surface homogeneity. The entire analysis reaffirms the suitability of $V_2O_5$ nanofibers as one of the futuristic sensing material for IR imaging applications.

## 1. Introduction

Strongly correlated materials like vanadium oxides have attracted much attention among the material scientists ever since the pioneering work of Morin [1], highlighting their phase transition behavior at Neel temperature. It has been reported that, vanadium oxides compounds (such as $VO_2$, $V_2O_3$, $V_2O_5$, etc.) undergoes a transition from a semiconducting state at low temperature to a metallic state at higher temperature; which is accompanied by an abrupt and fascinating change in their electrical, optical and structural properties [2]. Among these oxides, $VO_2$ and $V_2O_5$ have been extensively studied, as their transition temperatures are nearby room temperature, at around 67 °C–68 °C range. At the transition temperature, the electrical resistivity undergoes a drastic change (of the order of $10^5$) over a temperature interval of 0.1 °C, and in addition, simultaneously there is an abrupt change in their infrared transmission characteristics [3]. These features make $VO_x$ films, an ideal material for thermal sensing and optical switching applications [4]. $VO_x$ thin films are thus excellent materials for diverse technological applications such as uncooled IR microbolometer, optical and holographic storage systems, thermochromics coating, laser scanners, fiber-optical switching devices, ultrafast switching, and smart radiator devices for spacecraft [2].

An uncooled IR microbolometer belongs to the thermal sensor family. Primarily there are two types of IR detectors: Photon detectors and Thermal detectors. Photon detectors are also called cooled IR detectors, since they need to be cooled down to cryogenic temperature such as 77 K or lower, for their proper operation. Uncooled IR microbolometer belongs to a class of thermal detectors, which can be operated at room temperature without the need for cryogenic coolers; therefore they are called uncooled infrared detectors. Moreover, uncooled IR detectors have many advantages such as low cost, low weight requirement, low power, large spectral response, and long term operation when compared with photon detectors. Therefore, worldwide there is a growing interest in the development of uncooled IR microbolometer due to their wide range of applications ranging from military and civilian night vision, to space, to the detection of flames of fire alarms, the detection of heat emitted by warm objects for intruder detection, and in medicine, to mention just a few of the multifarious applications. A microbolometer is a temperature dependent electrical resistor, whose resistance will change when its temperature changes. In this regards, a wide variety of materials such as metals (Au, Pt, Ti, etc.) [5,6], semiconductors ($VO_x$, a-Si, etc.) [7,8] and superconductors have

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been reported as possible active elements for microbolometer. However, it is mostly the semiconductors which show higher TCR (defined as $TCR\% = \frac{1}{R}\frac{dR}{dT}*100$, where $R$ and $T$ represents the resistance and temperature) when compared with other materials. Since, the performance of a microbolometer is dependent on various parameters such as IR absorption, TCR, device resistance, thermal isolation, and noise properties. Of all these parameters, TCR and the device resistance are particularly important factors for achieving high detectivity in microbolometer. Considering the above material parameters, we have chosen vanadium oxide in this work due to its high TCR at room temperature and relatively low noise.

It is known that vanadium has different forms of oxide such as di, tri, and pentavalent states, because of its half-filled d-shell. Out of which, vanadium pentoxide ($V_2O_5$) has a most stable oxidation state in the V-O system. Moreover, $V_2O_5$ has attracted huge interest due to its unique structural, optical and electronic properties [9]. Based on various reports, there are several techniques to produce vanadium pentoxide thin films such as spray [10], thermal [11], pulsed laser deposition [12], RF/DC magnetron sputtering [13,14], electron beam evaporation [15], and hydrothermal synthesis [16], among others. However, there have been very less studies on fabrication of vanadium pentoxide nanofibers using chemical synthesis process by electrospinning technique. In recent studies several reports exploring vanadium oxides for infrared detection. But, most of reports related to vanadium oxides and multilayer vanadium oxides thin films in which TCR% is varying from − 2 to − 4% [17–19]. In case of nano fibers there are very few reports on multi walled carbon nano tubes [20] but there are no reports on vanadium oxide nano fibers for IR detectors. Hence, this study could give an idea of vanadium oxide nanofibers for infrared detector. Moreover, the advantage with electrospun $V_2O_5$ nanofibers is its simplicity with which microbolometer can be fabricated in few process steps. Besides that, they have higher surface to volume ratio, which will enhance the infrared sensitivity.

In our present study, we have developed a simple, robust and economical electrospinning process for making vanadium pentoxide nanofibers. Thereafter the nanofibers are extensively analyzed using various material characterization methods like XRD (for verifying its crystallinity), XPS (for verifying its elemental compositions) UV–Visible Spectrometry (for bandgap determination), Raman Spectroscopy (for molecular identification), SEM and AFM (for microstructure and surface topography analysis). The thermal and electrical characterization were performed to determine their response/recovery time and other infrared sensing properties such as TCR and responsivity, respectively to determine their suitability for IR sensing applications.

## 2. Experimental procedure and characterization techniques

### 2.1. Synthesis of polymer fibers

High purity chemicals such as Polyvinyl Alcohol (PVA) ($M_W$ 80,000) and Ammonium Metavanadate ($NH_4VO_3$) purchased from Sigma-Aldrich Inc. were used for making electrospinning polymer solution. Twenty milliliters of aqueous PVA solution with a concentration of 10 wt% was prepared by dissolving PVA powder in deionized water. The mixer was then heated under vigorous stirring condition at 80 °C, for a duration of 6 h. Subsequently, about 0.5 g of Ammonium Metavanadate ($NH_4VO_3$) was added to the above PVA solution. After the mixer had been stirred at 80 °C for about 4 h duration, a clear viscous light yellow solution of Ammonium Metavanadate/PVA was obtained. The mixed polymer solution was then filled in a syringe tube having a 24 gauge needle with an inner diameter of 0.55 mm for electrospinning process. During the Electrospinning process, a strong electric field of magnitude 154 kV/m was maintained between the needle and the collector, by keeping the needle and the collector 13 cm apart. The polymer solution inside syringe tube gets ejected like a polymer jet through the needle at a constant flow rate of 1 ml/hour till the end of the process. The polymer jet so collected onto the collector plate transforms itself into a mat of nanofibers after the evaporation of the associated solvents. The collected nanofibers were then heated at 550 °C for about two hours duration in a box furnace with a heat rate of 1 °C/min. The crystalline phases of the synthesized nanofibers were verified by powder X-ray diffraction (XRD) with Cu $K_\alpha$ radiation at 40 kV and 30 mA (PAN analytic X'pert pro). The chemical state of the metal oxide nanofibers were measured using X-ray photoelectron spectroscopy. The bandgap of the material was measured using UV–Visible spectrometer. A Raman spectrum was measured at room temperature using a Laser Micro Raman spectrometer (Bruker, Senterra). Microstructural examination of nanofiber samples was done using Scanning Electron Microscopy (SEM, ZEISS EVO-18). Surface analyses of nanofibers were investigated by Atomic Force Microscopy (Bruker make). Electrical I-V characteristics were measured by the two-probe method (Keithley 4200 SCS). A wide spectral band IR lamp was used during IR based electrical characterization of nanofibers.

## 3. Results and analysis

### 3.1. Structural properties

The nanofibers were calcined at different temperatures in order to identify its effect on their crystallinity. At 450 °C, the fibers show mixed phases of vanadium oxides such as $VO_2$, $V_2O_3$, $V_2O_5$, etc. Interestingly, after optimizing the calcination process when the fibers were calcined at 550 °C, they were showing a single phase crystalline structure consistently, as shown in Fig. 1. Analysis of XRD result confirms that the nanofibers have crystallized in monoclinic structure and their XRD pattern matches very well with the standard PCPDF reference number 01-075-6605. Moreover, the grain size is measured using Scherrer equation (= $(0.9*\lambda)/(\beta cos\theta)$, where $\lambda$ = 1.5406 Å for Cu $K_{\alpha 1}$ wavelength, $\beta$ = full width half maxima of the peak, $\theta$ = Braggs angle). The grain sizes are varying from 130 nm to 198 nm which is nearly equal to SEM results obtained for lower dimension of the $V_2O_5$ electrospun nanofibers.

The chemical composition of $V_2O_5$ nanofibers analyzed by XPS technique [21] is shown in Fig. 2. In order to determine various oxidation states of vanadium, such as $V_2O_5$, $VO_2$ and $V_2O_3$, corresponding to $V^{5+}$, $V^{4+}$ and $V^{3+}$ respectively, core level binding energies of $V2p_3$ are used, which are in a narrow range of about 515–530 eV. The core level spectrum of $V_2O_5$ has $V2p_{3/2}$, $V2p_{1/2}$ and O 1s peaks corresponding to the binding energies 517.26, 524.69 and 530 eV. From Fig. 2(b), the deconvolution of the $V2p_{3/2}$, $V2p_{1/2}$ and O 1s peak components performed to find the peak position. The peaks are deconvoluted into two peaks of $V2p_{3/2}$ at 517.26 and 515.56 eV together with $V2p_{1/2}$ at 524.69 and 523.02 eV corresponding to $V^{5+}$ and $V^{4+}$

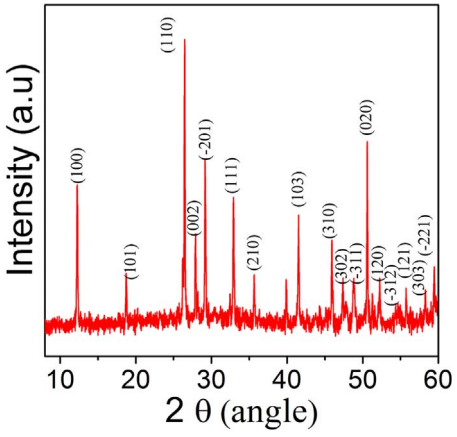


**Fig. 1.** XRD patterns of $V_2O_5$ nanofibers.