Sensors and Actuators A 279 (2018) 630–637

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Sol-gel deposition and characterization of vanadium pentoxide thin films with high TCR

Siamack V. Grayli [a,*], Gary W. Leach [b], Behraad Bahreyni [a]

[a] School of Mechatronic Systems Engineering, Simon Fraser University, Surrey, Canada
[b] Department of Chemistry, Simon Fraser University, Burnaby, Canada

ARTICLE INFO

Article history:
Received 14 April 2018
Received in revised form 30 June 2018
Accepted 1 July 2018
Available online 9 July 2018

Keywords:
Bolometric materials
IR sensing
Material characterization
Sol gel chemistry
TCR
Thin film deposition
Thin films
Vanadium pentoxide

ABSTRACT

Vanadium pentoxide thin films have been deposited on quartz substrates via sol-gel synthesis and dip coating. The process was developed to establish a reliable and inexpensive method to produce thin films with a high temperature coefficient of resistance (TCR) for sensing applications. Sol-gel precursor concentration and post-deposition annealing conditions were varied to address their effects on film composition, morphology, structure, resistivity, and TCR response. The resulting thin films were structurally characterized by thin film profilometry, x-ray diffraction, scanning electron microscopy, and Raman spectroscopy. Resistivity and TCR measurements were carried out to determine their efficacy as sensor materials. Both low and high concentration alkoxide sol-gel precursors led to films of pure α-V_2O_5 composition but with characteristically different structural and electrical properties. Low concentration films showed a modest decrease in resistivity and TCR with increasing annealing temperature, consistent with the formation of increasing grain size and the coalescence of largely planar grains with common crystalline orientation. In contrast, films fabricated from higher alkoxide precursor concentration are characterized by a higher density of grains with a larger dispersion in orientation and better-developed grain boundaries, leading to a general increase in resistivity and TCR with annealing temperature. The TCR of the films lied in the range of -3%°C^{-1} to -4%°C^{-1}, comparing favorably with films produced through conventional techniques such as DC magnetron sputtering, chemical vapor deposition, or pulsed laser deposition. Further, their TCR and resistivity characteristics can be controlled through sol-gel precursor concentration and post-deposition annealing temperature, indicating that sol-gel deposited vanadium pentoxide films are promising candidates for infrared sensor applications.

1. Introduction

Vanadium oxide has been the focus of widespread interest in industry and academia for its outstanding physical properties which include an insulator-to-metal phase transition [1], [2], reversible or irreversible crystalline lattice changes during thermal annealing [3–5], and a high temperature coefficient of resistance (TCR) [2,6]. The high TCR of vanadium oxide has resulted in its use in room-temperature infrared sensing applications [7–10]. A broad review of the common deposition techniques distinguishes between traditional vacuum methods that require a cleanroom setup for accomplishing the task versus room temperature methods whereby the deposition occurs through chemical processes that are carried at the ambient temperature. Variations of physical deposition techniques such as reactive ion beam sputtering, RF sputtering and e-beam evaporation are some of the most commonly employed methods to deposit vanadium oxide thin films [11–14]. The majority of these techniques produce films with TCR values in the range of -2%°C^{-1} to -3%°C^{-1}. Recent works in the field such as [15,16] have reported -3.5%°C^{-1} and -2.8%°C^{-1} TCR respectively. Amid the high uniformity of the deposited thin films, these methods bear high fabrication costs which are associated with cleanroom usage while offering limited increase in the TCR of the deposited thin films beyond the reported values. Concurrently, vacuum deposition methods cannot achieve stoichiometric compositions of vanadium oxide layers due to the existence of multiple phases in the vanadium oxygen phase diagram, therefore crystalline systems resulting from vacuum deposition methods result in sub-stoichiometric vanadium-oxygen crystalline structures that may result in less stable materials [5,17]. These techniques, also, yield little control over the oxidation state of the deposited films

* Corresponding author.
E-mail addresses: svgrayli@sfu.ca (S.V. Grayli), gleach@sfu.ca (G.W. Leach), bba19@sfu.ca (B. Bahreyni).

https://doi.org/10.1016/j.sna.2018.07.002
0924-4247/

and often create mixed oxide phases which can undergo physical phase transitions as the device heats up when irradiated by incident IR radiation [18–20]. Physical phase transitions, aside from introducing mechanical stress in the thin film, affect the charge transport characteristics of the thin film vanadium oxide [5]. Other phenomena such as the insulator-to-metal transition in VO_2 can also introduce abrupt changes in the deposited materials electrical properties over a narrow temperature range which can be undesirable for sensing applications above room temperature [5].

Both recently and in the past, researchers have investigated room temperature deposition methods such as spray pyrolysis, spin coating, drop casting and dip coating [21–24]. Due to the nature of the deposition techniques, these methods use a precursor that is synthesized prior to the thin film deposition. The TCR values for as-deposited thin films this way are not comparable to those from the vacuum techniques hence high temperature annealing is needed to increase the TCR values of the deposited films. Some of the recent works in the field are reported by [25,26] with TCR values of -1.4%°C^{-1} and -2%°C^{-1} for the as-deposited films. Annealing however increases the TCR values significantly. Of the two most studied cases, vanadium dioxide (VO_2) offers relatively higher TCR (∼ -4%°C^{-1}) yet is less stable whereas vanadium pentoxide (V_2O_5) offers slightly lower TCR (∼ -3.5%°C^{-1}) but is chemically stable [17,25,26]. Higher density of vanadium oxygen bonds in V_2O_5 results in broader IR absorption spectra hence make the material a more suitable choice for RT IR sensing applications [27–29]. It is therefore important to investigate methods to deposit vanadium pentoxide thin films with high purity that are not hampered by the mix oxide phase composition and Vanadium oxide has been the focus of widespread interest in industry and academia for its outstanding physical properties which include an insulator-to-metal phase transition [1,2], reversible or irreversible crystalline lattice changes during thermal annealing [3–5], and a high temperature coefficient of resistance (TCR) [2,6]. The high TCR of vanadium oxide has resulted in its use in room-temperature infrared sensing applications [7–10]. A broad review of the common deposition techniques distinguishes between traditional vacuum methods that require a cleanroom setup for accomplishing the task versus room temperature methods whereby the deposition occurs through chemical processes that are carried at the ambient temperature. Variations of physical deposition techniques such as reactive ion beam sputtering, RF sputtering and e-beam evaporation are some of the most commonly employed methods to deposit vanadium oxide thin films [11–14]. The majority of these techniques produce films with TCR values in the range of -2%°C^{-1} to -3%°C^{-1}. Recent works in the field such as [15,16] have reported -3.5%°C^{-1} and -2.8%°C^{-1} TCR respectively. Amid the high uniformity of the deposited thin films, these methods bear high fabrication costs which are associated with cleanroom usage while offering limited increase in the TCR of the deposited thin films beyond the reported values. Concurrently, vacuum deposition methods cannot achieve stoichiometric compositions of vanadium oxide layers due to the existence of multiple phases in the vanadium oxygen phase diagram, therefore crystalline systems resulting from vacuum deposition methods result in sub-stoichiometric vanadium-oxygen crystalline structures that may result in less stable materials [5,17]. These techniques, also, yield little control over the oxidation state of the deposited films and often create mixed oxide phases which can undergo physical phase transitions as the device heats up when irradiated by incident IR radiation [18–20]. Physical phase transitions, aside from introducing mechanical stress in the thin film, affect the charge transport characteristics of the thin film vanadium oxide [5]. Other phenomena such as the insulator-to-metal transition in VO_2 can also introduce abrupt changes in the deposited materials electrical properties over a narrow temperature range which can be undesirable for sensing applications above room temperature [5].

Both recently and in the past, researchers have investigated room temperature deposition methods such as spray pyrolysis, spin coating, drop casting and dip coating [21–24]. Due to the nature of the deposition techniques, these methods use a precursor that is synthesized prior to the thin film deposition. The TCR values for as-deposited thin films this way are not comparable to those from the vacuum techniques hence high temperature annealing is needed to increase the TCR values of the deposited films. Some of the recent works in the field are reported by [25,26] with TCR values of -1.4%°C^{-1} and -2%°C^{-1} for the as-deposited films. Annealing, however, can increase the TCR values significantly to about -4% [26]. Of the two most studied cases, vanadium dioxide (VO_2) offers relatively higher TCR (∼ -4%°C^{-1}) yet is less stable whereas vanadium pentoxide (V_2O_5) offers slightly lower TCR (∼ -3.5%°C^{-1}) but is chemically stable [17,25,26]. Higher density of vanadium oxygen bonds in V_2O_5 results in broader IR absorption spectra hence make the material a more suitable choice for RT IR sensing applications [27–29]. It is therefore important to investigate methods to deposit vanadium pentoxide thin films with high purity that are not hampered by the mix oxide phase composition and offer a broader IR absorption range for sensing applications [27,28]. Previous research has demonstrated the possibility of solution phase chemistry, such as sol-gel processes, for the synthesis of vanadium oxide and deposition methods such as dip coating or spray coating of non-planar surfaces to improve process repeatability [30–32]. Our work provides a thorough investigation of the development of high purity phase crystalline vanadium pentoxide thin films as well as a full structural and electrical characterization of the deposited films as a function of precursor concentration and temperature. Table 1 offers a comparison between what presented here and the previous work in the field.offer a broader IR absorption range for sensing applications [27,28]. Previous research has demonstrated the possibility of solution phase chemistry, such as sol-gel processes, for the synthesis of vanadium oxide and deposition methods such as dip coating or spray coating of non-planar surfaces to improve process repeatability [30–32]. Our work provides a thorough investigation of the development of high purity phase crystalline vanadium pentoxide thin films as well as a full structural and electrical characterization of the deposited films as a function of precursor concentration and temperature. Table 1 offers a comparison between what presented here and the previous work in the field.

We previously reported typical TCR values of -2.0%°C^{-1} for thin samples of less than 200 nm in thickness [37]. We also observed a thickness dependence of the TCR response as well as the resistivity of annealed samples to be generally larger than those not subject to annealing. However, our observations did not allow us to establish a well-defined link between sample thickness, TCR response, and film resistance. In this work, we present the use of sol-gel chemistry to synthesize pure phase vanadium pentoxide thin films. We have investigated the effects of alkoxide concentration in the pre-hydrolysis sol and film thickness as well as post-deposition film annealing on the formation of vanadium oxide thin films. We also present measurements on the thermo-electrical response of the films, which exhibit high TCR values needed for RT IR detection.

2. Experimental

Thin films of vanadium oxide were deposited onto 0.5 mm thick, 25 mm × 25 mm square quartz slides. Prior to deposition, the slides were cleaned with powdered soap and coarse brushing, rinsed with deionized water, sonicated in acetone and isopropyl alcohol (IPA), each for 30 min. The substrates were placed in a 120 °C oven and dried over 24 h prior to deposition to reduce uncontrolled