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Vanadium oxide thin films with high midwave & longwave infrared thermo-optic coefficients and high temperature coefficients of resistance

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ABSTRACT

The development of thermo-optic modulator elements for midwave infrared (MWIR) and longwave infrared (LWIR) electro-optic systems, and the development of resistive thermometer elements for infrared imaging microbolometers require materials with high thermo-optic coefficients *(TOC)* and high temperature coefficients of resistance (*TCR*), respectively. In this paper, we synthesize novel vanadium oxide (V_xO_y) thin film structures and measure their MWIR/LWIR thermo-optic coefficients (*TOC*s) and their temperature coefficients of resistance (*TCR*s). The V_xO_y thin film are synthesized by sputter depositing interchanging, 5 nm-thick, layers of vanadium sesquioxide (V_2O_3) and vanadium (V) reaching a final thin film thickness of 95 nm. The sputter deposited multilayer structures are then ex-situ annealed in N_2 and O_2 atmospheres at 300 °C for 30 min. Infrared spectroscopic ellipsometry was used to measure the optical constants of the thin films as a function of temperature across the MWIR and LWIR bands (3000–14000 nm). The synthesized V_xO_y thin films exhibited high *TOC*s and high *TCR*s when operated in their semiconducting phase. A high *TOC* was measured reaching a maximum of 0.0278 $^\circ C^{-1}$ and 0.119 $^\circ C^{-1}$ at $\lambda = 4000$ nm for N_2 and O_2 annealed V_xO_y thin films respectively; and reaching a maximum of 0.0634 $^\circ C^{-1}$ and 0.139 $^\circ C^{-1}$ at $\lambda = 10{,}000$ nm for N_2 and O_2 annealed V_xO_y thin films respectively. Moreover, sheet resistance versus temperature measurements were conducted revealing room temperature sheet resistances of 1.495 k Ω/sq. and 1.516 k Ω/sq. and *TCR*s of −3.54%/°C and −3.46%/°C for N_2 and O_2 annealed V_xO_y thin films respectively.

1. Introduction

Various vanadium oxide compounds are known to undergo insulator to metal phase transitions at certain temperatures, across which the optical and electrical properties of the compound are greatly altered [1]. As a consequence of the drastic change in the optical and electrical properties, high thermo optic coefficients (*TOC*s) as well as a high temperature coefficients of resistance (*TCR*s) are expected; a fact that led vanadium oxide compounds to be employed in many modern solid

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state devices. The *TOC* is a parameter that quantifies the amount of change in refractive index, *n*, as a function of a given temperature, *T*, change [2]. *TOC* is given by:

$$TOC(\lambda) = \frac{dn(\lambda)}{dT} \tag{1}$$

And the *TCR* describes the amount of change in resistance, *R*, due to change in temperature, *T*. The *TCR* is expressed as [3]:

$$TCR = \frac{1}{R}\frac{dR}{dT} \tag{2}$$

Numerous studies investigated the electrical properties across the insulator to metal phase transition and in specific in the semiconductor phase region where the *TCR*s of some vanadium oxide compounds are very high. This successfully led to developing vanadium oxide microbolometers for thermal imaging applications [4–6]. Furthermore, several studies explored the thermo-optic properties and exploited the high *TOC*s of vanadium oxide thin films in the near infrared (NIR) band for applications such as: micro-optical switches for fiber-optic telecommunication systems [7], and smart windows for solar radiation control [8]. On the other hand, fewer studies investigated the midwave infrared (MWIR) and longwave infrared (LWIR) thermo-optic properties of vanadium oxide thin films. In [9], the thermo-optic transmission contrast properties of doped vanadium dioxide (VO_2) thin films in the LWIR band were examined for using the thin films as a micro-shutters in electro-optic civilian and military surveillance systems. In addition, VO_2 thin films were used as miniaturized smart mirrors in dual band LWIR detectors in [10], and as LWIR optical shutters in protective windows for sensitive IR detectors in surveillance imagers against harmful incoming laser radiation [11]. The above described studies [9–11] were mainly focused on characterizing and using vanadium oxide thin films in the on/off switching mode between the insulator and the metal phases with no quantification of their *TOC*s in the semiconducting phase. The assessment and quantification of the *TOC*s of vanadium oxide thin films in the MWIR and LWIR bands complements the above studies, and contributes to gaining more insight about the thermo-optic properties of vanadium oxides, and also helps promoting the use of vanadium oxides as functional materials in MWIR and LWIR electro-optic systems requiring high *TOC* performance. In addition, investigating the MWIR and LWIR *TOC* properties of vanadium oxides helps presenting them as alternatives for silicon (Si)-based materials currently being used in MWIR and LWIR thermo-optic modulators [12,13] with applications in sensing, MWIR and LWIR telecommunications, and infrared countermeasures.

The work presented in this paper aims to investigate the MWIR and LWIR thermo-optic properties and the thermo-electric properties of novel vanadium oxide (V_xO_y) thin films synthesized by interchanged vanadium sesquioxide/vanadium (V_2O_3/V) multilayer deposition followed by ex-situ annealing. The interchanged multilayer synthesis technique was successfully introduced in previous studies [14–18] and it relied on depositing interchanged multilayers of a vanadium oxide compound (such as: V_2O_5 and V_2O_3) and V metal; and then ex-situ annealing the deposited multilayer structure at different annealing temperatures and atmospheres leading to a V_xO_y thin film containing multiple phases of vanadium oxide compounds and having desired electrical properties: a high *TCR* and a low electrical resistivity. The conducted studies in [14–18] have shown that this synthesis technique allowed controlling the resistivity and *TCR* values of the synthesized V_xO_y thin films via varying the annealing conditions as well as varying the ratios between the thicknesses of the vanadium oxide compound (V_2O_5 and V_2O_3) layers and the V layers. It is, thus, expected that a V_xO_y thin films prepared by the above described technique, which allows process-controlling the electrical properties of the formed thin films and yields high *TCR*s, would likewise possess process-controllable optical properties and high *TOC*s.

In this paper, we synthesize and characterize, optically and electrically, novel V_xO_y thin film structures synthesized by ex-situ annealing magnetron sputtered interchanging multilayers of V_2O_3 and V. Infrared spectroscopic ellipsometry is used to measure the optical constants, *n* and *k*, of the V_xO_y thin films as a function of temperature. The *TOC*s of the thin films are evaluated at 4000 nm and 10,000 nm. Temperature-dependent sheet resistance measurements are also conducted and the *TCR*s of the developed thin films are evaluated.

2. V_xO_y Thin film preparation method

The $(V_2O_3/V)^9/V_2O_3$ multilayer thin film structure was sputter deposited on an Si substrate above which a 300 nm layer of silicon dioxide (SiO_2) was deposited for thermal insulation, which is required for sheet resistance versus temperature measurements. The thin film structure is composed of 18 interchanged layers of V_2O_3 and V each having a thickness of 5 nm above which a final V_2O_3 layer was deposited. The V_2O_3 layers were RF sputter deposited from a 99.5% pure V_2O_3 target at 150 W of power and a deposition rate of 0.68 nm/min. And the V layers were DC sputter deposited from a 99.9% pure V target at 150 W of power and a deposition rate of 4 nm/min. Both V_2O_3 and V layers were sputter deposited at 3 mTorr of argon pressure and at a sputter-chamber base pressure of 4.48×10^{-6} Torr. Two different samples of the deposited multilayer thin film structure were then separately ex-situ annealed in a horizontal tube furnace at 300 °C for 30 min. in nitrogen (N_2) and oxygen (O_2) atmospheres at a gas flow rate of 120 ml/min. The annealing process is meant to cause oxygen atoms to diffuse from oxygen rich V_2O_3 layers to the thin metallic V layers; and as a result, a V_xO_y thin film is formed containing multiple phases of vanadium oxide compounds, as concluded in [14–18]. In addition, annealing in O_2 atmosphere is purposed to introduce more O_2 atoms within the thin film structure and thus producing V_xO_y thin film with different thermo-electric