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Manufacture and characterization of sol–gel $V_{1-x-y}W_xSi_yO_2$ films for uncooled thermal detectors

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Abstract

$V_{1-x-y}W_xSi_yO_2$ films for uncooled thermal detectors were coated on sodium-free glass slides with sol–gel process, followed by the calcination under a reducing atmosphere (Ar/H_2 5%). The $V_{1-x-y}W_xSi_yO_2$ films as prepared inherit various phase transition temperatures ranging from 20 to 70 °C depending on the dopant concentrations and the fabrication conditions. Compared to the hysteresis loop of plain VO_2 films, a rather steep loop was obtained with the addition of tungsten components, while a relaxed hysteresis loop with the tight bandwidth was contributed by Si dopants. Furthermore, the films with switching temperature close to room temperature were fabricated to one-element bolometers to characterize their figures of merit. Results showed that the $V_{0.905}W_{0.02}Si_{0.075}O_2$ film presented a satisfactory responsivity of 2600 V/W and detectivity of 9×10^6 cm $Hz^{1/2}$/W with chopper frequencies ranging from 30 to 60 Hz at room temperature. It was proposed that with appropriate amount of silicon and tungsten dopants mixed in the VO_2, the film would characterize both a relaxed hysteresis loop and a fair TCR value, which effectively reduced the magnitude of noise equivalent power without compromising its performance in detectivity and responsivity.

Keywords: $V_{1-x-y}W_xSi_yO_2$ film; Thermochromic; Sol–gel process; Uncooled thermal detector; Detectivity; Responsivity

1. Introduction

Infrared (IR) detectors were classified as photon or thermal detectors, depending on their response to electromagnetic radiation [1]. Photon detectors have characteristics of outstanding signal-to-noise ratios (S/N) as well as fast response time since photons interact directly with the electrons bonded to the lattice atoms of a detector [2]. However, a photon detector must work with a cryogenic cooler to meet with the operating temperature of the detector [3]. In contrast, thermal detectors such as bolometers exhibit a change in physical or electrical properties when responding to the incidence of electromagnetic waves. As a result, they have no impressive S/N sensitivity and responsivity when compared with that of the photon detectors. Yet, thermal detectors have the phase transition temperature close to room temperature, which give them better mobility and comparatively low operating cost [4].

Vanadium dioxide, one of the thermochromic materials, characterized a reversible metal insulator transition (MIT) at 68 °C with a structural transformation from monoclinic to tetragonal phase. VO_2 has good electrical characteristics such as high temperature coefficient of resistance (TCR) values in phase transition, favorable electrical resistance, and low signal noise [5]. Vanadium dioxide can be manufactured by methods including atmospheric-pressure chemical vapor deposition [6], pulsed laser deposition technique [7], reactive magnetron sputtering [8], and sol–gel method [9]. Different fabrication processes affected the magnitude of the electrical resistance, shapes of hysteresis loops and the phase transition temperature in different extents, depending on the film quality, grain size, and atomic stoichiometry. It was reported that the switching temperature of vanadium oxide could be altered by doping the high-valent or low-valent

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cations. The doping of tungsten demonstrated a remarkable decreasing rate of −26 K/at.% W, while the doping of fluorine gave a reduction of transition temperature by −20 K/at.% F, rhenium −18 K/at.% Re, and molybdenum −12 K/at.% Mo, respectively [10,11]. All these dopants behaved like donors to the V 3d valent band, which made the V^{4+}–V^{4+} pairs relaxed. In consequence, charge transfer due to the transformation of V^{4+}–V^{3+} pairs and M^{x+}–V^{3+} pairs along the *a*-axis crystalline destabilized the monoclinic phase of vanadium dioxide. Thus, their metal–insulator transition temperatures were reduced by the addition of dopants [12]. Furthermore, the effects of dopants in vanadium dioxide not only caused the switching temperature to change but also influenced the transmittance, grain size, and width of hysteresis loop. The hysteresis loop widths of $V_{1-x}Mo_xO_2$ (x = 0–0.041) films prepared by dual-target sputtering (V and Mo) were claimed to decrease from 31 °C (for x = 0) to 5 °C (for x = 0.041) by the addition of Mo [13]. In addition, thermal annealing was reported to be beneficial to the restoration of thermochromism in the implanted films and the sharp increase of transmittance curve upon the phase transition was achieved [14].

In this study, various ratios of sol–gel precursors (Si^{y+}/V^{3+}, W^{x+}/V^{3+}) were mixed at three different concentration levels according to the design of experiments and they were calcined in reducing atmosphere (Ar/H_2 5%) within a tube furnace. The films with good temperature-dependent electrical properties and fair switching temperature were made to one-element bolometers by lithographic and metallization processes for further device characterization. Three parameters, responsivity (R_v), noise equivalent power (NEP), and detectivity (D^*) were examined at a bias current of 10 μA under various chopper frequencies. These parameters are defined as follows:

$$R_v(T, f) = \frac{V_s}{\varphi(T)} = \frac{I_b R\alpha\eta}{G\sqrt{1+\omega^2\tau^2}}, \quad (1)$$

where $R_v(T, f)$ represents the output signal voltage in response to input radiation from a black-body at absolute temperature T, with the signal measured at frequency f. V_s is the root-mean-square (RMS) signal voltage at output of a detector of area A in response to incident radiation of RMS power $\varphi(T)$. I_b is the bias current, R the electrical resistance, η the absorptivity of $V_{1-x-y}W_xSi_yO_2$ film, G the thermal conductance, ω the chopper frequency, α the TCR, and τ the thermal time constant [15]. In addition, NEP represents a signal-to-noise ratio and is determined by

$$\mathrm{NEP} = \frac{V_n}{R_v}, \quad (2)$$

where V_n is defined as the root-mean-square noise voltage and R_v is the output signal voltage responding to incident radiation. Besides, the detectivity of a detector is defined as

$$D^*(T, f) = \frac{\sqrt{A_d \Delta f}}{\mathrm{NEP}} = \frac{R_v\sqrt{A_d \Delta f}}{V_n}, \quad (3)$$

where A_d is the active detector area and Δf is the electrical bandwidth in Hz.

Table 1
Summary of mixing ratios of tungsten and Si dopants for each $V_{1-x-y}W_xSi_yO_2$ group

$V_{1-x-y}W_xSi_yO_2$ composite films		Mixing ratios	
Case	Abbreviation	$X = W^{x+}/V^{4+}$	$Y = Si^{y+}/V^{4+}$
A	VO_2	0	0
B	$V_{0.925}Si_{0.075}O_2$	0	0.075
C	$V_{0.85}Si_{0.15}O_2$	0	0.15
D	$V_{0.99}W_{0.01}O_2$	0.01	0
E	$V_{0.915}W_{0.01}Si_{0.075}O_2$	0.01	0.075
F	$V_{0.84}W_{0.01}Si_{0.15}O_2$	0.01	0.15
G	$V_{0.98}W_{0.02}O_2$	0.02	0
H	$V_{0.905}W_{0.02}Si_{0.075}O_2$	0.02	0.075
I	$V_{0.83}W_{0.02}Si_{0.15}O_2$	0.02	0.15

2. Experiment

Vanadium oxy-triethoxide (Aldrich) was mixed with isopropanol as well as acetic acid and stirred for 24 h. The viscosity of the gel solutions was controlled around 1.8 ± 0.1 cP before spin coating to maintain a consistent film thickness. The vanadium oxide thin films were then calcined under reducing atmosphere (Ar/H_2 5%) at 550 °C for 2 h at a ramping rate of 10 °C/min. Dopants such as tungsten oxy-chloride (Aldrich) and TEOS (Aldrich) were added into vanadium sol–gel solutions based on the design of experimental methodology shown in Table 1. The film thickness of all prepared films was measured by the Tencor Alpha-Step surface profiler. Sheet resistance of thin films was characterized by Keithley 2400 sourcemeter, modulated by a four-point probe tool. The morphology of composite films was evaluated by atomic force microscope (Digital Instruments Nanoscope IIIa).

The one-element bolometer was patterned as 5 mm × 5 mm sensitive area by wet etching, and the Au metallization was deposited by sputtering. The characterization of IR absorbing layer as prepared was implemented without using air-gap suspending structure. A black-body furnace was operated at 773 K as a thermal source for the bolometer. In addition, a mechanical chopper chopped the input radiation, and the responded output signal and noise were recorded by a lock-in amplified (EG&G 7260) with various chopper frequencies under a bias current of 10 μA. The detailed schematic diagram of the apparatus is illustrated in Fig. 1.

3. Results and discussion

3.1. The morphology of VO_2 composite films

The film thickness of all VO_2 films was 152 ± 13 nm measured by the Tencor Alpha-Step surface profiler. The morphology of the deposited films was examined by atomic force microscope (DI Nanoscope IIIa) operating in a tapping mode. The grain sizes and surface roughness were measured at five different locations in each specimen. The mean values of the grain size and surface roughness for cases A–I are summarized in Table 2. The plain VO_2 film in case A has a surface roughness of 2.26 nm and grain sizes ranging from 20 to 40 nm with the