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# Comparative study of annealing and gold dopant effect on DC sputtered vanadium oxide films for bolometer applications

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**Abstract** Vanadium oxide ($VO_x$) thin film has been widely used for IR detectors and it is one of the promising materials for THz detectors due to its high temperature coefficient of resistance (TCR) values. $VO_x$ films with proper TCR values have also high resistance and it restricts bolometer performance especially for uncooled bolometers. To overcome this problem, deposition at elevated temperatures or annealing approach has been accepted and used but gold co-deposition approach has been proposed recently. In this study, vanadium oxide films were fabricated on high resistivity silicon substrates by reactive direct current magnetron sputtering in different $O_2$/Ar atmosphere at room temperature. We investigated influence of oxygen partial pressure during deposition process and fabricated $VO_x$ thin films with sufficient TCR values for bolometer applications. In order to decrease resistivity of the deposited films, post annealing and gold doping approaches were performed separately. Effect of both post annealing process and gold doping process on structural and electrical properties of $VO_x$ thin films deposited at room temperature were investigated and detailed comparison between these methods were presented. We obtained the best possible approach to obtain optimum conditions for the highly reproducible $VO_x$ thin films which have the best resistivity and suitable TCR value for bolometer applications.

**Keywords** Vanadium oxide · Gold doping · TCR · Magnetron sputtering · Post annealing

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## 1 Introduction

Bolometers are frequently used detectors in the terahertz and infrared region hence demand for bolometers which are more sensitive and have fast response time over a wide operating range has increased greatly. According to their operation temperatures bolometers can be divided into two: Uncooled and cooled. Cooled detectors are usually fabricated from superconducting materials (Semerci et al. 2016) and they are highly sensitive and fast, but they need expensive cooling systems. In contrast to cooled ones, uncooled detectors operate at room temperature (RT) and they have low power consumption. One of the crucial requirements of the low noise uncooled bolometer is high temperature coefficient of resistance (TCR) and low Johnson noise (Johnson 1928) which is related to resistivity. Many metals can be used as sensitive material for bolometers such as Bi (Uchida et al. 2007) and Ti (Gilmartin et al. 2008) but their TCR values are between 0.1 and 0.3% 1/K which is not in range of applicable bolometer TCR values that is from near −2 to −3% 1/K (Wang et al. 2013). On the other hand, vanadium oxide (Rogalski 2011) and amorphous silicon (Ajmera et al. 2010) are two dominant materials in the security and military applications such as night vision, mine detection and surveillance.

Most of the vanadium oxide ($VO_x$) phases have metal insulator transition (MIT) induced by heat and light. Although there are many other phases that are well known like $V_2O_3$, $V_3O_5$ and $VO_2$, $V_6O_{11}$, there are also less known phases like $V_5O_9$ and $V_8O_{15}$ that have MIT at individual temperatures. They can be categorized and formulized into two group which are $V_nO_{2n+1}$ and $V_nO_{2n-1}$ also known as Magneli phases (Magneli 1948). One of the most prominent vanadium oxide phase is $VO_2$ which has a MIT at 68 °C along with four order of magnitude resistivity change. Although $VO_2$ has four orders of magnitude resistance change around MIT temperature its hysteresis and high resistance properties restrain its detection capability. $VO_x$ film has a stable TCR over a wide range temperature and its resistance values can be reduced with doping metal such as gold (Smith et al. 2014). Moreover $VO_x$ has low 1/f noise and suitable thermal time constant with low manufacturing cost (Rogalski 2009). Due to these advantages $VO_x$ thin films have been used as bolometer material at IR and they have been obtained by several different techniques that include reactive sputtering (Kusano et al. 1988), evaporation (Case 1984), metal organic decomposition (Son et al. 2012), RF magnetron sputtering (Castro et al. 2013), pulsed laser deposition (Narayandas et al. 2003) and sol–gel methods (Dachuan et al. 1996). Even though there can be employed many diverse methods to fabricate $VO_x$ thin films, acquiring desired electrical and optical properties is still a challenge because many oxide phases of vanadium are not stable. Moreover even a slight change in oxygen partial pressure or temperature change during production will effect film properties enormously. DC magnetron sputtering has been preferred because it provides large area uniformity and high deposition rate. TCR values of $VO_x$ thin films vary in the literature (Chen et al. 2006; Dai et al. 2008; Wang et al. 2013). The reason behind acquiring various TCR values is related to deposition techniques, deposition or post annealing temperatures and oxygen partial pressure during deposition. It has been a common agreement that suitable $VO_x$ thin films for bolometer applications must have resistivity below 10 Ω cm with a TCR near −2% 1/K (Fieldhouse et al. 2009). Studies showed that higher TCR values (Yuqiang et al. 2007) can be achieved but reproducibility of these films are also important. Gold doping solution has been proposed recently (Smith et al. 2014) to solve high resistance problem of $VO_x$ films, but work mostly focused on bolometer application at

IR region. We propose a comparison between this new approach and old one such as post annealing for sensitive THz bolometers.

In this paper, we focused on changes in the electrical properties as well as structural properties of dc sputtered $VO_x$ thin films just after annealing or gold doping. In addition to that $VO_x$ films with different oxygen partial pressures were fabricated at room temperature then post annealing was performed. Hence oxygen partial pressure and post annealing effect on TCR were also investigated. All the process including post annealing was performed under 400 °C in quartz furnace nitrogen environment therefore it is also compatible with CMOS technology. Moreover, we reported that a certain amount of co-sputtering gold during $VO_x$ deposition decreases film resistance accompanied with slight change of film composition and TCR, but it did not degrade film surface.

## 2 Experimental

$VO_x$ thin films were deposited on high resistivity floating zone silicon (HRFZSi) (100) by DC reactive sputtering at room temperature. Substrates which have thickness of 0.5 mm were cut into $1 \times 1$ $cm^2$ size and native oxides of silicon substrates were removed with 10% HF then $SiO_2$ layer was thermally grown by dry oxidation at air ambient. Chamber is evacuated to a base pressure of $5 \times 10^{-6}$ Torr just before deposition. In order to obtain contaminant free target surface, 10 min presputtering was performed prior to deposition. $VO_x$ thin films were grown at $Ar/O_2$ mixed gas pressure environment at room temperature and constant sputtering power. High purity (99.95%) vanadium target was used. Substrates were rotated at 15 RPM in order to improve the uniformity of the film growth. Schematic

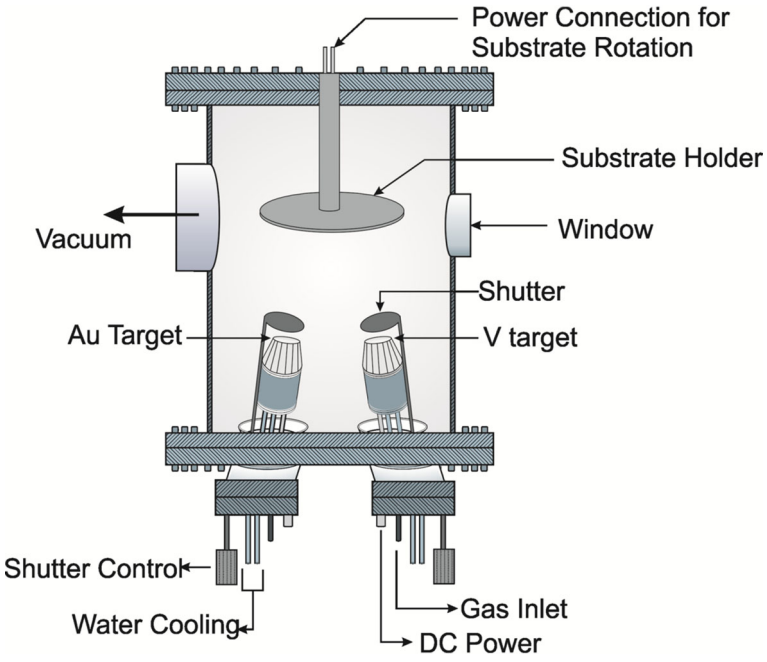


**Fig. 1** Schematic representation of DC magnetron sputtering system

representation of DC magnetron system is shown in Fig. 1. In the first part of the experiment oxygen gas ratio of the sputtered thin films was changed and electrical properties of the films were investigated. In the second part deposition conditions which provided the best TCR value were kept same and small amount of Au was doped during deposition then electrical properties of the films were investigated after doping. Sputtering conditions for all the films were given in the Table 1 below.

Structural and morphological properties of the films were evaluated by field emission scanning electron microscopy Philips Quanta and X ray diffraction was recorded by X Ray diffractometer (XRD) Philips PAN analytical X'Pert XRD System using Cu $K_\alpha$ radiation with a step size of 0.04°. Thickness of the films were measured by SEM crosssectional images and confirmed by spectroscopic ellipsometry. Electrical measurements were performed and electrical properties of $VO_x$ samples were characterized between 295 and 350 K on a microprobe station (Janis Microprobe Station). Data was acquired with Keithley multimeter and automatically recorded using Lab View program.

## 3 Results and discussion

### 3.1 SEM analysis

Surface morphologies of the $VO_x$ thin films were investigated and SEM images of the films were shown in Fig. 2. In contrast to $VO_2$ dominated thin films, as deposited $VO_x$ thin film surface is smooth. After annealing, films oxide phases and surface morphology of the films were changed. It can be seen in Fig. 2a that film surface is very smooth before anneal which is crucial for lithographic steps and it is an imperative property for bolometer construction. The film may consist of nano grains just before annealing and these grains coalescence into bigger ones which is about 200 nm average size of diameter. Although grain shapes and diameters vary by many conditions which are related to substrate, buffer layer and growth temperature, there has been similar report in the literature (Dou et al. 2015) that indicate annealing is the main driving force to form bigger grains. SEM crossection image is shown in the Fig. 2c and it is taken for confirming film thickness and silicon oxide layer thickness. We successfully optimized the thickness of the $VO_x$ film for bolometric applications on the top of the $SiO_2$ support layer. Thickness of $SiO_2$ layers were also confirmed by spectroscopic ellipsometer. It is clear that after post annealing, $VO_x$ film surface on silicon substrate (Fig. 2b) becomes similar to $VO_2$ on sapphire substrates which deposited at elevated temperatures like 550 °C (Fig. 2d) after annealing in terms of grain shapes and size. Their respective average grain sizes are 200 nm for annealed $VO_x$ films and 350 nm for $VO_2$ films. In contrast to annealed $VO_x$ films, $VO_x$:Au films which were fabricated by DC magnetron sputtering at RT also had same flat surfaces like as grown $VO_x$ films.

**Table 1** Deposition parameters of $VO_x$ thin films

| Deposition conditions | Value |
|---|---|
| Substrate temperature | Room temperature |
| DC sputtering power | 50 W |
| Sputtering time | 30 min |
| Base pressure | $5 \times 10^{-6}$ Torr |
| Working pressure | $3 \times 10^{-3}$ Torr |

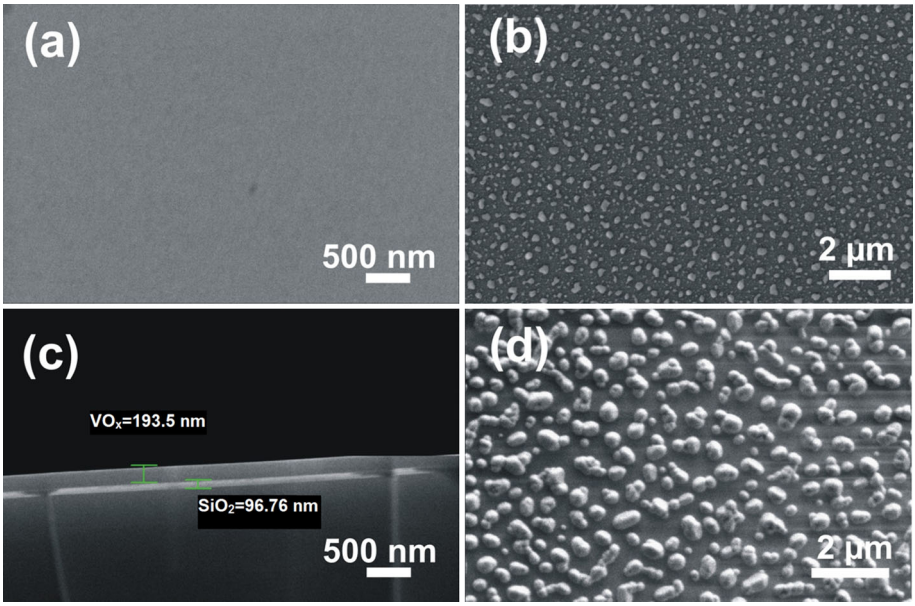


**Fig. 2** **a** As grown $VO_x$ multi oxide phase thin film fabricated at room temperature **b** annealed $VO_x$ thin film **c** cross sectional image of $VO_x$ film **d** $VO_2$ dominated films fabricated at 550 °C on sapphire substrate

### 3.2 XRD analysis

The XRD diffraction spectrum was collected from 10° to 65° and influence of annealing as well as doping effect on the film composition was investigated. The corresponding XRD patterns of as grown thin films, annealed and doped thin films are shown in Fig. 3. It was observed that both $VO_x$ and $VO_x$:Au thin films exhibit multi oxide phase structures. $VO_x$ thin films mainly consist of $V_2O_5$ phase along with small portion of $VO_2$ and $V_6O_{13}$ phases before annealing process. As shown in Fig. 3 diffraction peaks with solid circles could be indexed to orthorhombic pentoxide (JCPDS card no 41-1426) and with solid stars could be indexed to vanadium dioxide (JCPDS card no 43-1051). It can be seen that $VO_x$ film prepared on silicon oxide buffer layer has been consisted of poly crystalline structure with nano sized grains. It can also be seen that diffraction peak 16.7° which is related to (200) $V_2O_5$ intensity decreased and 61.6° which is related to (042) $V_{16}O_3$ increased just after annealing both for $VO_x$ and $VO_x$:Au thin films. It is showed that accompanying decrease in the x value was the main cause of formation of lower oxide phases just after annealing. It can be seen that $V_2O_5$ which is a higher oxide phase and has $x = 2.5$ reduce to $V_6O_{13}$ which is a lower oxide phase and has $x = 2.2$. It could be explained that lower oxide phases are more stable for temperature increment than higher oxide phases. In addition to that doping gold into $VO_x$ thin films caused a slight change in structural composition of the films. Gold doped $VO_x$ films consisted of more $V_6O_{13}$ phase and less $V_2O_5$ than undoped $VO_x$ films. In other words gold doping decreased x value and restricted to form higher oxide phases in the $VO_x$ film. Annealing had the same effect on $VO_x$:Au films and annealed $VO_x$:Au films contain lower oxide phases such as $V_2O_3$ and $V_6O_{13}$.

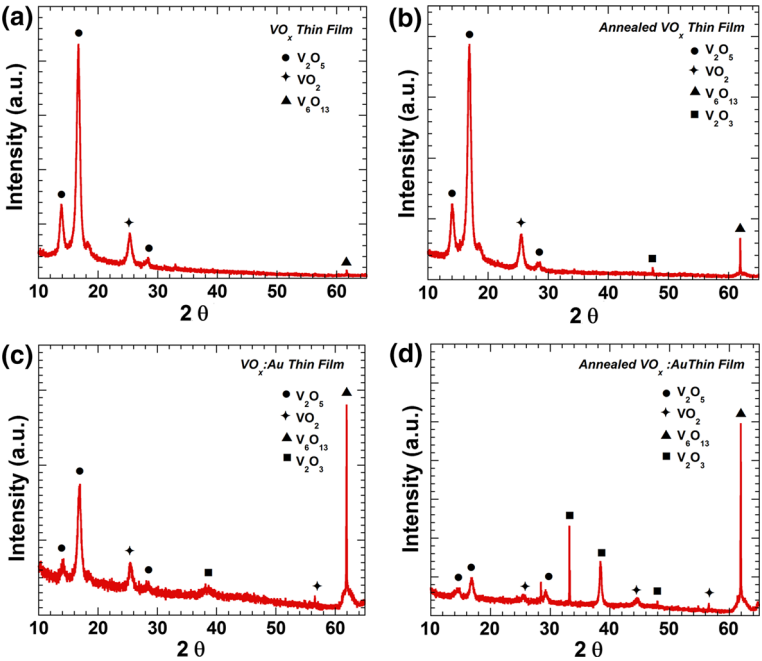


**Fig. 3** **a** X-ray diffraction pattern of as grown $VO_x$ thin film **b** annealed $VO_x$ thin film **c** as grown $VO_x$:Au thin film **d** annealed $VO_x$:Au thin film

### 3.3 Electrical properties

It is known that complex phases of vanadium oxide films have been widely used at IR region for bolometer applications and in order to improve their performance they need to be optimized with precise controlling of sputtering parameters. TCR is one of the crucial parameters that effects detector performance and it is calculated using the equation below

$$\alpha = \frac{1}{R}\frac{dR}{dT} \tag{1}$$

where the α is the TCR, R is the resistance of the film and T is the temperature. It represents the value of resistance change with temperature and it is directly related to responsivity and detectivity values of a detector which are given in the equations below

$$R_V = \frac{\alpha\eta I_B R_0}{G\sqrt{1+\omega^2\tau^2}} \tag{2}$$

$$D = \frac{R_V\sqrt{A_d\Delta f}}{V_n} \tag{3}$$

where η is the absorptivity, $I_B$ is the bias current applied to device, $R_0$ is the bolometer resistance at room temperature, G is the thermal conductance, ω is the modulation frequency, τ is the thermal time constant, $A_d$ is the detector area, Δf is the bandwidth and $V_n$ is the signal noise. Time constant is related to heat capacity and it could be optimized.

$$\tau = \frac{C}{G} \tag{4}$$

where C is the heat capacity. Ideal bolometer responsivity must be maximum and time constant must be minimum. It is obvious that high TCR is beneficial for bolometer response. In addition to that reducing heat capacity and increasing thermal conductance are needed for acquiring minimum time constant. Heat capacity is related to film thickness and thicker films have large thermal capacity because of that 65–200 nm film thickness is usually chosen for bolometer applications (Wang et al. 2006, 2013). In this work film thickness of the films were also optimized to 150 nm. Variation of electrical resistivity of nonlinear curve fitted $VO_x$ thin films between 295 and 350 K temperature for the films deposited with different oxygen partial pressures are shown in Fig. 4 and related TCR values for each film are listed in Table 2. Measurement result of $VO_x$ film with 8% oxygen partial pressure and its nonlinear curve fitting are given as inset at Fig. 4a.

It can be seen that increasing oxygen partial pressures of the film in the deposition process causes TCR increment of the films. Similar behavior was observed in the literature (Subrahmanyam et al. 2008) at room temperature DC sputtered $VO_x$ thin films. Oxygen partial pressures during deposition were calculated with equation below.

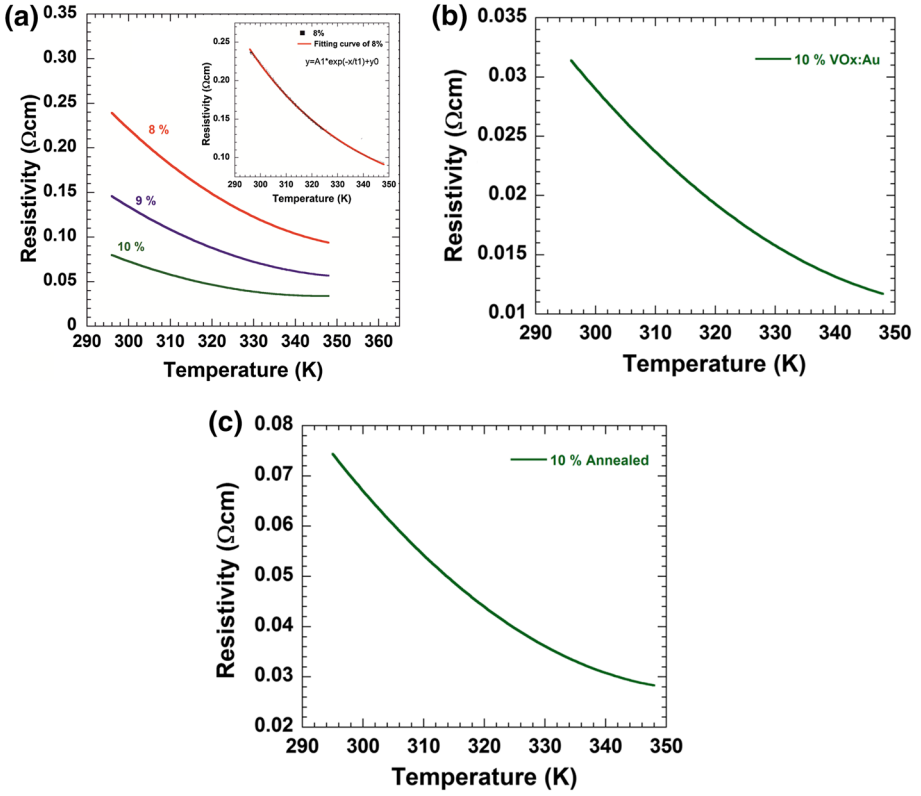


**Fig. 4** **a** Effect of different oxygen partial pressures during deposition and gold doping on $VO_x$ thin films (*Inset* nonlinear curve fitting of $VO_x$ film with 8% oxygen partial pressure) **b** effect of gold doping **c** effect of annealing

**Table 2** Oxygen partial pressure, doping and post annealing effect on TCR of the films

| $\rho_{Oxygen}$ oxygen partial pressure (%) | Gold doping | Annealing | TCR (−%) |
|---|---|---|---|
| 8 | – | – | 1.54 |
| 9 | – | – | 1.60 |
| 10 | – | – | 1.77 |
| 10 | Performed | – | 1.67 |
| 10 | – | Performed | 1.55 |

$$\rho_{Oxygen} = [\text{Oxygen(sccm)}]/\,[(\text{Argon(sccm)}) + (\text{Oxygen(sccm)})] \quad (5)$$

Although obtained TCR values are attractive for bolometer applications resistivity values can be decreased by gold doping. Because higher resistivity value causes higher Johnson noise value which is an essential noise for uncooled bolometer and is described below.

$$V_{rms} = \sqrt{4k_B TR\Delta f} \quad (6)$$

where T, R, $k_B$ and $\Delta f$ are the resistor's temperature, resistance, Boltzmann constant and the bandwidth respectively. To overcome high resistivity problem, doping with different metals was studied by different groups (Smith et al. 2014; Han et al. 2005). But detailed comparison for post annealing, gold doping and oxygen partial pressure has not been presented.

Optimum TCR value −1.77% 1/K was achieved at 10% oxygen partial pressure at room temperature deposition. It was also observed in Figs. 4c and 2b that post annealing decreases film resistivity but increases film surface roughness. Gold doping was performed for the film which has the best TCR value and it decreases resistivity of the film significantly without altering film surface.

It is observed that film resistivity with optimum TCR value can be decreased with gold doping without sacrificing TCR value. Fabricated films are highly reproducible and stable. Resistivity decrease is observed up to 10% oxygen partial pressure and above this point resistivity increases. This electrical behavior also supports previous finding in the literature (Subrahmanyam et al. 2008).

## 4 Conclusion

Vanadium oxide thin films were prepared by DC magnetron sputtering method at room temperature. The best approach was investigated for achieving high TCR and low resistivity values. It is concluded that increasing TCR at constant temperature and sputter voltage is possible with increasing oxygen partial pressure during sputtering process. It is found that obtaining stable and highly reproducible $VO_x$ thin films with highest TCR value and lowest resistivity is possible with 10% oxygen partial pressure and 9% wt gold doping at constant sputtering power without in situ or post annealing process. It is assumed that excessive heating during deposition is needed to obtain higher oxide phases in the structure accompanied with high oxygen partial pressure to obtain even higher TCR values.

Although optimized gold doping altered film composition slightly, it caused forming lower oxide phases more than higher oxide phases in the $VO_x$ films. It is concluded that gold doping is the best alternative to overcome high resistance problem comparing to post annealing in the $VO_x$ films but it must be carefully optimized.

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