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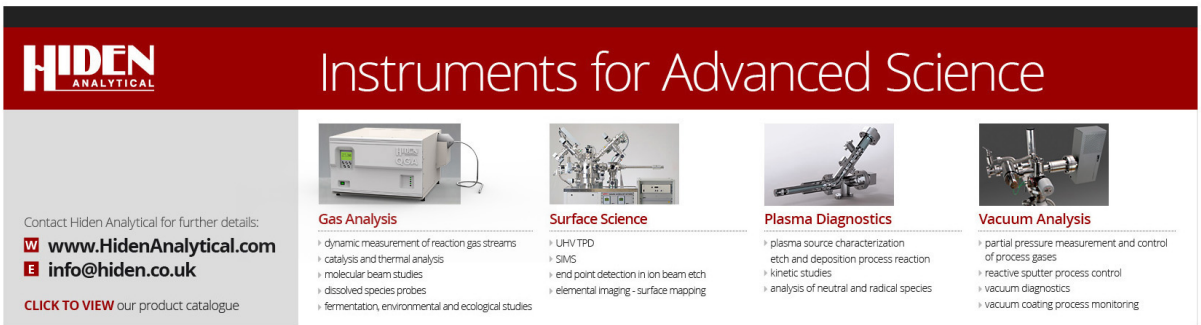
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Atomic layer deposition synthesized TiO_x thin films and their application as microbolometer active materials

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This paper demonstrates the possible usage of TiO_x thin films synthesized by atomic layer deposition as a microbolometer active material. Thin film electrical resistance is investigated as a function of thermal annealing. It is found that the temperature coefficient of resistance values can be controlled by coating/annealing processes, and the value as high as −9%/K near room temperature is obtained. The noise properties of TiO_x films are characterized. It is shown that TiO_x films grown by atomic layer deposition technique could have a significant potential to be used as a new active material for microbolometer-based applications. © *2016 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4947120]

I. INTRODUCTION

Uncooled microbolometers have been promoted as a low-cost infrared imaging solution for applications such as thermography, firefighting, and surveillance in the past. Figure 1(a) shows the schematic of a standard microbolometer. Such a microbolometer typically consists of an infrared-absorbing layer, a thermally sensitive active layer, a structural material for mechanical support, and a CMOS read-out circuit. The absorption of the incoming infrared radiation increases the temperature of the active layer behaving as a temperature-dependent resistor. Subsequently, the change in the resistance is detected via a standard read out integrated circuit, translated into an electrical signal, and then converted into an image. Recent trends show skyrocketing mobile devices industry with rapidly growing demand for novel functionalities such as thermal imaging. Smart home concepts are spearheading the demand on low cost thermal imaging solutions. New materials with high temperature coefficient of resistance (TCR) values and CMOS compatible process technologies are sought after. Atomic layer deposition (ALD) is a standard technique in silicon CMOS for high-k dielectric deposition. Therefore, ALD based thin films are quite attractive as next generation active materials of microbolometers.[1] One of the most important parameters of active materials is the temperature coefficient of resistance.

TCR is defined as the percent change of a material's electrical resistance R with unit temperature difference[2]

$$\mathrm{TCR} = \frac{1}{R} \times \frac{dR}{dT}.$$

It is desired that the bolometer active material assures a high TCR value preferably exceeding 2%/K, an adequate resistivity to match the read-out electronics, low 1/f-noise, the ability to be deposited using a technique compatible with the existing microbolometer fabrication processes, and stable electrical properties.[3]

To date, several materials have been used as active layers of microbolometer such as vanadium oxide (TCR value up to 2–3%/K),[4] amorphous silicon (1–4%/K),[5] silicon–germanium (3–4%/K),[2] graphene (3–4%/K),[6] zinc oxide (10.4%/K),[7] Ti (0.25%/K),[8] poly SiGe (1.9%/K),[9] and YBaCuO (3.2%/K).[10] Among others, vanadium oxide (VO_x) and amorphous silicon (a-Si) are widely accepted standard materials for traditional microbolometers. Meanwhile, there are quite many efforts for finding alternative materials with higher efficiency, lower process cost, and superior output.

Titanium oxide is a large-band gap semiconductor with significant applications in corrosion-resistant coating, pigment, photocatalysis, solar cells, medical implants, thermal isolation layers, and optical active coatings.[11–13] TiO_x can be an attractive alternative as bolometric material. Recent research efforts have indicated that TiO_x films can appear in different phases based on the deposition and annealing

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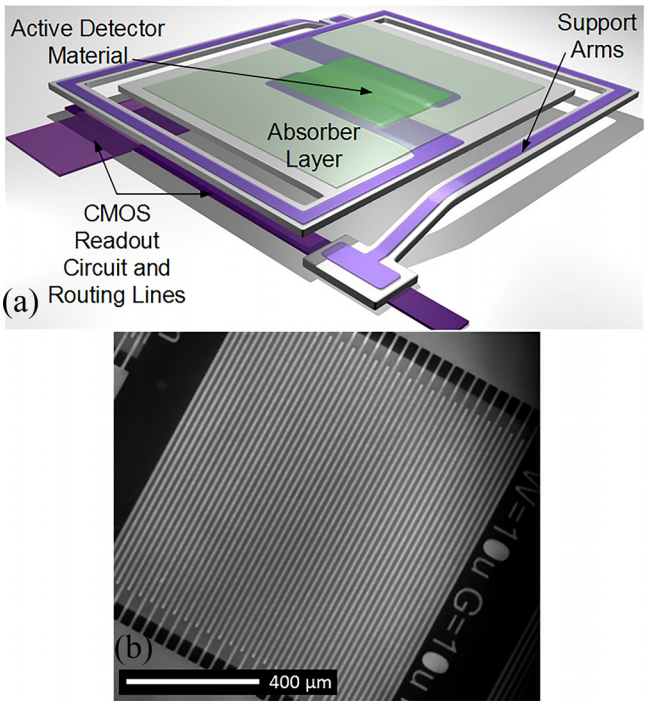


FIG. 1. (Color online) (a) General structure of an uncooled infrared microbolometer detector. (b) SEM image of the successfully produced resistance structure.

conditions, and the structural and electrical properties vary greatly under thermal annealing. Consequently, the resistivity and temperature coefficient of resistance of titanium oxide films can be changed by many orders of magnitude by varying the deposition and annealing parameters.[13–15]

There are numerous methods including sol–gel process, chemical vapor deposition, thermal evaporation, and reactive magnetron sputtering that can be used to prepare titanium oxide films. However, there are quite few TCR characterization of TiO_x films which are mostly deposited by RF reactive magnetron sputtering as well as DC sputtering. Kwon *et al.*[16] investigated reactively sputtered TiO_x films and obtained TCR value up to 2.8%/K. Reddy *et al.*,[14,17] with the same deposition technique but different oxygen content, obtained the TCR value up to 3.66%/K. TiO_x films prepared by Jiang *et al.*[13] via reactive DC sputtering showed a TCR value of 3.3%/K. In this work, we introduced low-temperature ALD of TiO_x layers together with annealing processes. ALD is a deposition technique in which the introduction of different precursors is separated by intermittent evacuation and/or purging steps.[18] This method is attractive due to its self-limiting growth, which enables the deposition of highly conformal and uniform thin films with monolayer thickness control over large areas and high aspect ratio structures. Nanometer-thick layers enabled by ALD have a significant potential to enhance the performance of bolometers by fulfilling low thermal conductance and near ideal optical properties. In the Experiment section the fabrication of TiO_x thin films by ALD is presented, succeeded with material and electrical characterizations in Results and Discussion section.

II. EXPERIMENT

Following standard cleaning of a silicon substrate, it is immediately settled into the chamber and ALD process is started. The ALD process is performed using a Cambridge Nanotech, Inc., Savannah S100 reactor. Tetrakis(dimethylamido)titanium(IV) (TDMAT) and milli-Q water (H_2O) are employed as reaction precursors for titanium and oxygen, respectively. The TDMAT precursor is kept at 75 °C during the deposition. A single TiO_x processing cycle involves a 100 ms TDMAT pulse, 1 min N_2 purging followed by 15 ms H_2O pulse and 1 min N_2 purging. Due to the low deposition temperature, the extended purging periods are applied to enhance the film's quality. The resulting self-limiting TiO_x film deposition rate is derived to be 0.4 Å/cycle. For TiO_x depositions, N_2 is used as the carrier gas with the flow rate of 20 sccm. In order to observe the effects of growth and annealing temperatures, the films are deposited at temperatures of 150, 200, and 250 °C and annealed subsequently at various temperatures (300, 330, 475, 550, and 600 °C) preferred based on thermogravimetric analysis (TGA), for 1 h in a conventional furnace, in air ambient.

X-ray diffraction (XRD) measurements of film grown at 150 °C are performed in a PANalytical X'Pert PRO MRD diffractometer using Cu Kα radiation. XRD patterns are obtained by performing ten repeated scans within the 2Theta range of 20°–80° with a step size of 0.1° and counting time of 10 s. X-ray photoelectron spectroscopy (XPS) are carried out using Thermo Scientific K-Alpha spectrometer with a monochromatized Al Kα x-ray source. Pass energy, step size, and spot size are 30, 0.1 eV, and 400 μm, respectively. With respect to the adventitious carbon peak located at 284.8 eV, high-resolution XPS data were corrected for charging by shifting peaks. Peak deconvolution was performed using the ADVANTAGE software, without applying any restrictions on the spectral location and full width at half maximum values.

For TCR measurements, interdigitated finger-type electrode structures are fabricated by standard optical lithography, BCl3-based dry etching of TiO_x, and thermal evaporation of metal contacts. Figure 1(b) shows an SEM image of a completed resistor structure. TCR measurements are carried out using a temperature controlled heating stage where the temperature is varied between 15 and 40 °C, while voltages across the resistors are recorded by applying a current between 1 and 10 μA. Noise measurements are performed by applying a current of 3 μA on the resistors and measuring the voltage on the resistor with the help of an amplifier and a dynamic signal analyzer. Noise power spectral densities of the resistors are obtained at the end of the measurements, and 1/f noise corner frequencies are calculated.

III. RESULTS AND DISCUSSION

A. Material characterizations

Figure 2 shows grazing incidence x-ray diffraction patterns of as-deposited TiO_x thin films and annealed at different temperatures. According to these results, as-deposited film is amorphous while by increasing temperature above 300 °C, the

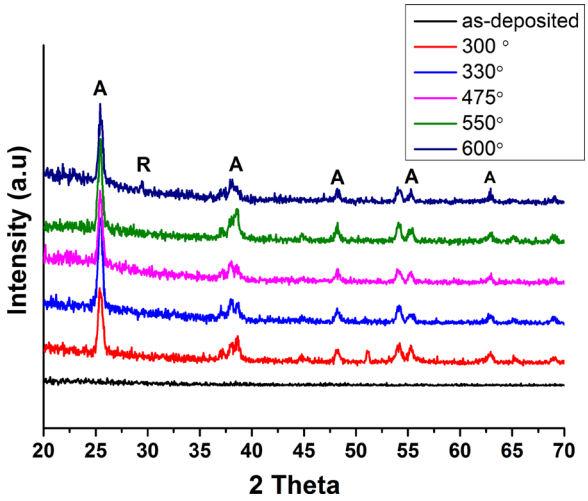


FIG. 2. (Color online) X-ray diffraction patterns of TiO_x films annealed at various temperatures. A, anatase phase; R, rutile phase.

crystalline phase of anatase appears. The intensity of (101) anatase phase is increasing with the annealing temperature, indicating the formation of a more crystalline film. The structural characteristics of these films are hardly observed because of the very low-intensity of x-ray signals. This is a result of small x-ray scattering due to the ultrathin structure. In spite of this fact, we recognized a low intensity diffraction of (110) from the rutile phase of the films annealed at 600 °C. However, based on TGA and XPS analysis, it seems that the phase transition of anatase to rutile occurs at 475 °C. Hanaor *et al.*[19] reported that the onset temperature of thermally activated transformation from anatase to rutile was dependent on experimental parameters such as deposition methods, deposition temperature, and different substrates.

In order to determine the stoichiometry of TiO_x films, survey scan and detailed analysis of O1s spectra are used. Figure 3(a) shows XPS survey scan spectra of TiO_x annealed at different temperatures. There is C1s spectra at 285 eV due to the surface contamination considered as standard reference line, and Ti2p and O1s spectra are adjusted in accordance with this energy. Due to the binding of O–H and O–Ti, O1s spectra consist of two peaks. Peak shifts are clarified by vertical lines corresponding to the bonding energy of O–Ti and O–H at 530 and 531.6 eV, respectively. Because of water vapor used as the precursor, hydroxyl groups can be detected. Figure 3(b) shows high-resolution O1s spectra. Two peaks, which belong to O–Ti and O–H bonding states, are used to fit the O1s spectra.[20–23] Table I shows elemental ratios obtained by fitting O1s spectra. The ratio of O:Ti increases with the rise of the temperature. As a result, the oxygen stoichiometry in TiO_x varied from 1.80 to 1.84 with respect to the annealing temperature. At 475 °C, the highest value of O:Ti ratio is observed due to the diffusing oxygen filling in vacancies. By the presence of rutile above this temperature, O:Ti ratio slightly decreases.[24]

B. Electrical characterization

Resistivity measurements revealed that TiO_x films' resistivity value depends on the coating and annealing

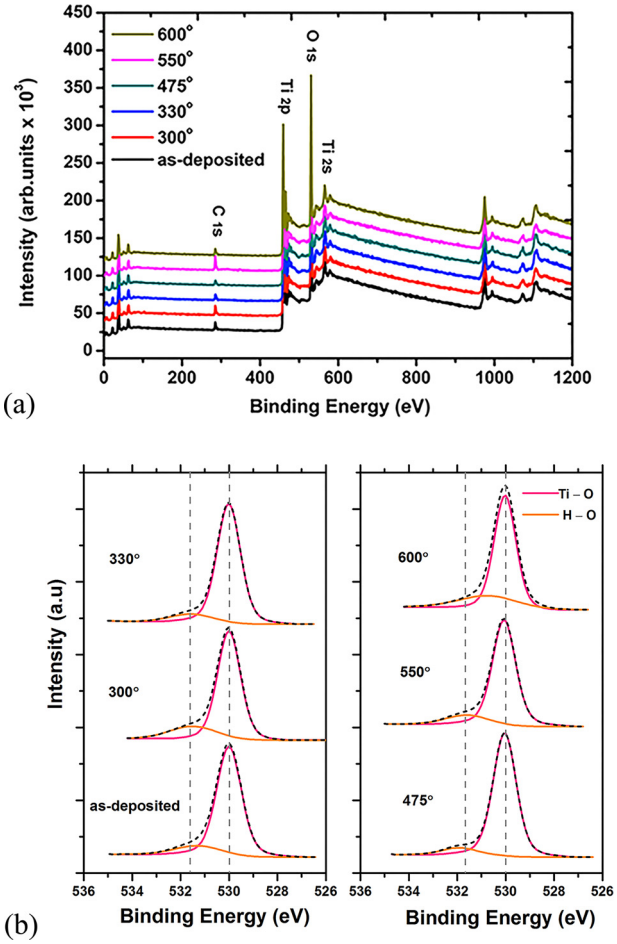


FIG. 3. (Color online) (a) Wide scan survey x-ray photoelectron spectra of TiO_x films annealed at various temperatures. (b) Detailed O1s analysis of TiO_x films as-deposited and annealed at various temperature.

TABLE I. Composition of ALD-grown titanium dioxide films annealed at various temperatures.

Annealing temperature (°C)	O/Ti ratio (±0.01)
As-deposited	1.80
300	1.81
330	1.81
475	1.84
550	1.83
600	1.83

TABLE II. Resistivity values of TiO_x film based on coating/annealing temperatures.

Coating/annealing temperature (°C)	Resistivity values (Ω cm)
150/without annealing	6.4×10^{-3}
150/300	4.5×10^{-4}
150/330	9.2×10^{-4}
150/475	4.7×10^{-4}
150/550	3.8×10^{-4}
150/600	2×10^{-3}
200/without annealing	8.4×10^{-3}
250/without annealing	6.4×10^{-3}

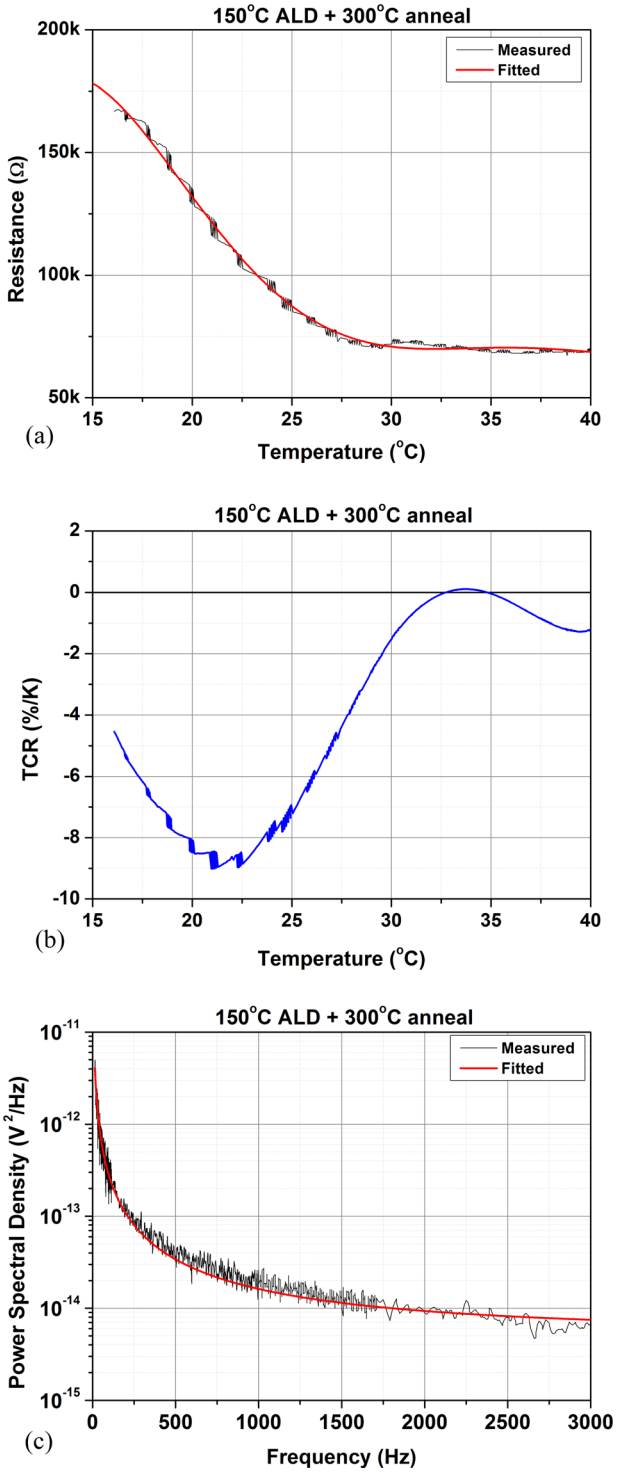


FIG. 4. (Color online) (a) Temperature variation of fabricated resistance, (b) TCR value and (c) noise power spectral densities of the same TiO_x resistance coated/annealed at 150 °C/300 °C.

temperature. As it is shown in Table II, the resistivity value decreases by annealing due to more ordered crystalline structure and decrease in oxygen defects (confirmed by XPS results).[17] However, the effect of coating temperature on the resistivity change is not much noticeable.

Figures 4(a) and 4(b) show the measurement results of the resistance and the TCR values of the resistor fabricated using thin film TiO_x coated/annealed at 150 °C/300 °C [see supplementary Fig. 4s(a) and 4s(b)].[25] Temperature variation during the fabrication strongly affects the TCR value of the films. The results also indicate that the TCR of the grown films strongly depends on the measurement temperature. Table III shows the maximum TCR values of the TiO_x resistors, measured between 20 and 30 °C, and TCR value at 25 °C. By controlling annealing temperatures, it is possible to achieve higher TCR values. The mixed phases (anatase and rutile) in samples annealed at low temperatures (300 and 330 °C) can result in metastable films whereas those annealed at high temperatures (475 °C and above) exhibit consistent trends with annealing temperature. As it is observed in Table III, TiO_x film grown at 150 °C and annealed at 300 °C has the highest TCR value of −9%/K, which is much higher than the TCR value of active layers used in commercial microbolometers.

TABLE III. Maximum TCR value between 20 and 30 °C and TCR value at 25 °C based on coating/annealing temperatures.

Coating/annealing temperature (°C)	TCR value at 25 °C (%/K)	Maximum TCR value between 20 and 30 °C (%/K)
150/without annealing	−1.12	−1.3
150/300	−7.2	−9
150/330	−1.13	−1.32
150/475	−6.56	−6.6
150/550	−5.46	−7.9
150/600	−8.63	−8.68
200/without annealing	−2.47	−2.5
250/without annealing	−2.08	−2.1

Active layers with low electrical noise are supposed to accomplish high sensitivity and detectivity in microbolometers. Dominant components of the electrical noise in microbolometers are primarily flicker noise and thermal noise. The spectral noise analyses of the grown films have been performed on resistors patterned on such films. Noise measurements performed for samples with high TCR value and low resistivity, since it is difficult to measure the noise under certain current for high value resistors. Accordingly, the noise measurements cover TiO_x film grown at 150 °C and annealed at 300 and 475 °C, which have high TCR values as well.

Figure 4(c) shows the noise power spectral density of the thin film TiO_x resistors. The corner frequency of TiO_x annealed at 300 and 475 °C found to be 1.8 and 1.2 kHz, respectively, which is compatible with the corner frequencies of many microbolometer materials [see supplementary Fig. 4s(c)]. The flicker noise is lower at higher annealing temperature due to enhanced crystallinity and lower defects in TiO_x films.

IV. SUMMARY AND CONCLUSIONS

In conclusion, we have investigated the TCR and electrical noise of ALD-grown TiO_x thin films with respect to the annealing temperature effect and its usage in uncooled microbolometers. Coating and annealing are performed at various temperatures to observe the effect of the growth temperature on the properties of the TiO_x. Anatase–rutile transition for ALD deposited TiO_x was observed to be around

475–500 °C. The film grown at 150 °C and annealed at 300 °C has a high TCR value (−9%/K) compared to commercial active layers, and the results of electrical noise investigation verify the film as a practicable material. Therefore, ALD-grown TiO_x films can be regarded as a promising candidate on employing as the active layer materials for commercial microbolometers.

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