**TOPICAL REVIEW**

**TiO$_{2-x}$ films for bolometer applications: recent progress and perspectives**

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**Abstract**

The bolometer is widely used in military and civilian infrared imaging due to its advantages of non-cooling, small size and portability. Thermosensitive materials seriously affect the performance of bolometers. As a kind of heat-sensitive material, the TiO$_{2-x}$ material has the advantages of good thermal stability, large-area preparation, and compatibility with the complementary metal-oxide semiconductor (CMOS) process. However, there is almost no review on the application of titanium oxide for bolometers. In this paper, we introduce the bolometer’s main thermal and photoelectric performance parameters and the critical technologies to manufacture the bolometer. Finally, we will particularly emphasize the effects of preparation process parameters of TiO$_2$ on the performance parameters temperature coefficient of resistance (TCR), 1/f noise, etc.

**1. Introduction**

A bolometer is a thermal detector based on the absorption of thermal radiation, which changes sensitive materials’ resistance. The first bolometer device was carried out around radiation metrology as early as 1880 [1], and its application to infrared imaging has been a matter of recent decades. Putley fully described the thin film bolometer’s infrared detection principle and established a theoretical model of response and noise limit in 1966 [2]. However, the following matter is that the bolometer’s size is large, which could not be made into an array device. In 1987, Johnson proposed using the anisotropic processing of silicon technology to create a silicon nitride thin-film microbridge structure for the thermal detector insulation structure [3]. Until 1992, Honeywell Research Center successfully manufactured a microbolometer uncooled infrared imaging device [4]. After that, a microbolometer can be widely used in night driving assistance systems for vehicles and ships, security monitoring, building energy-saving detection, industrial temperature measurement, and environmental monitoring, etc. The bolometer device has three main issues: absorbing radiation energy by absorb structure, keeping absorbed energy by thermal isolation structure, and converting the energy to an electric signal by the heat-sensitive material. To achieve a high-performance bolometer, a heat-sensitive material with a high temperature coefficient of resistance (TCR), low noise, and adaptable resistance is necessary.

In recent years, a few kinds of heat-sensitive materials have been developed. Vanadium oxide (VO$_x$), amorphous silicon (a-Si), and carbon nanotubes (CNTs) are widely accepted heat-sensitive materials due to their high TCR and affordable noise level. These materials have high TCR (of approximately 2 $\sim$ 3 $\%$/K for VO$_x$ [5], 1 $\sim$ 4 $\%$/K for a-Si [6] and CNT for 0.26 $\%$/K [7]) and suitable noise characteristics (1/f noise parameter: low $10^{-13}$ for VO$_x$, low $10^{-11}$ for a-Si) for bolometer. However, VO$_x$ has a drawback of its unstable reproducibility because it undergoes a phase change caused by the heating
process that occurs after the formation of the oxide film [8]. The a-Si is known for its high 1/f noise, which is detrimental to the bolometer [9, 10]. The diameter of CNTs will essentially affect the width of the material band gap [7]. If the CNTs with inappropriate diameter are used as the surface adsorption material of the detector element, it will affect the infrared absorption of the detector. Refer to table 1 for relevant parameters.

As a metal oxide semiconductor, titanium dioxide (TiO$_2$) has attracted much attention because of its nontoxic, high chemical stability, high dielectric coefficient, diverse and straightforward preparation methods [16]. TiO$_2$ is widely used in sensitized solar cells, gas sensors, resistance switch storage, photocatalysis and memristor [17–21]. TiO$_2$ can be widely used in these fields related to its structure and properties [16]. Non-stoichiometric titanium oxide (TiO$_{2-x}$) means that Ti has different chemical states Ti$^{3+}$ and Ti$^{4+}$, corresponding to Ti$_2$O$_3$ and TiO$_2$. Ti$_2$O$_3$ is a conductive material, while TiO$_2$ is an insulator with a high resistivity of about 10$^8$ Ω·cm. In comparison, TiO$_{2-x}$ with excess titanium is an N-type semiconductor with unique electrical properties [22]. Recently, it has been reported that non-stoichiometric TiO$_{2-x}$ films can be used as thermistor materials for the uncooled bolometer [23, 24]. At the same time, through research, TiO$_{2-x}$ has a good application in radiometers [25]. Therefore, scientists at home and abroad have made outstanding achievements in improving the electrical performance of titanium oxide materials. Reddy et al [8] studied the influence of various factors on TiO$_{2-x}$ films for bolometric properties. The author reported the influence of thermal annealing at 300 °C on the TiO$_{2-x}$ sample, indicating that a small decrease of the bandgap was observed and the 1/f noise parameter, resistivity, and TCR were also decreased. The TCR of the TiO$_{2-x}$ film samples can get up to 3.66 -%/K with a 1/f noise parameter for 1.89 × 10$^{-11}$. They successfully investigated the effect of the oxygen partial pressure and Nb doping on the TiO$_{2-x}$ film properties. They found that with the oxygen partial pressure increasing, the resistivity was increased, which resulted in the enhancement of TCR value for about 3.6 -%/K [22]. The Nb-doped TiO$_{2-x}$ films showed a controllable resistivity, low 1/f noise parameter for 10$^{-12}$, and relatively high TCR value for 3.1 -%/K [25]. Tanrikulu et al [26] synthesized the TiO$_{2-x}$ thin films by atomic layer deposition grown at 150 °C and annealed at 300 °C, which has a very high TCR for 9 -%/K Ju et al [27, 28] fabricated amorphous TiO$_{2-x}$ thin films at room temperature by controlling the substrate temperature and oxygen partial pressure, the films’ electrical properties could be adjusted with the O/Ti ratio changed from 1.73 to 1.97, and the TCR of the samples also varied from 1.2 to 2.3 -%/K. Based on material research, Kwon et al [29] reported the first TiO$_{2-x}$ films based 50 μm pitch microbolometer with the NETD of 34 mK. Jeong et al [30] reported TiO$_{2-x}$ based on the focal plane array with an array size of 640 × 480 pixels and 1024 × 768 pixels in 2018, the noise equivalent temperature difference (NETD) and time constant for the VGA detector were 40.5 mK and 8.5 msec, respectively. TiO$_{2-x}$ has been widely studied in recent years because of its easy availability, environmental friendliness and good stability in harsh environment. Therefore, in recent years, many scientists have attracted in-depth research on TiO$_{2-x}$ material films. Therefore, TiO$_{2-x}$ is a potential substitute for mainstream bolometer thermal sensitive materials at this stage.

2. Bolometers: main characteristics and tradeoffs

2.1. Heat flow equation

All thermal IR detectors exhibit a change in some measurable property that accompanies a change in the sensitive element’s temperature: the picture element caused by the absorption of IR radiation by the pixel. A bolometer infrared detector’s basic principle is to use thermally sensitive detection materials whose resistance value changes correspondingly with the temperature changing.

The infrared detector has measurable characteristics, which change with the temperature of the sensitive element. The two-dimensional component thermal pixel is composed of a single focal plane array. Each thermal pixel is connected with the support substrate. Its structural diagram is shown in figure 1. The thermal sensitive material covered by each pixel area absorbs infrared radiation and increases its temperature, so that the heat flows from the sensitive area to the surrounding environment.

There are three common heat transfer mechanisms: conduction, convection and radiation: heat can flow from the sensitive area and its support to the substrate. If the sensitive area is continuous, heat flows from the sensitive area of one pixel to adjacent pixels, which is called transverse heat flow. Try to avoid this situation in the design of the thermal detector because it will reduce the solution of the image. If the array is not installed in a vacuum package, heat will flow through the surrounding atmosphere. In general, the effect of heat transfer on the thermal array is not considered because the array package is usually empty. In addition, if the array package does not empty the gas, the heat loss of the sensitive element is usually through conduction rather than convection. At present, the main heat loss mechanism is radiation, and the array is at the background limit, which is the basic limit of its performance.
| Materials Preparation methods | Optimization methods | TCR ($\times 10^{-3}$) | $1/f$ noise parameter ($V^2 \cdot Hz^{-1}$) |
|--------------------------------|----------------------|-----------------------|----------------------------------------|
| VO$_x$ Reactive ion sputtering  | Annealing between 296 K and 310 K | 6.5                   | 7.49 x 10$^{-1}$                        |
| VO$_x$ DC reactive sputtering | Annealing at 400°C   | 2.8                   | 2.93                                    |
| a-Si Plasma enhanced chemical vapor deposition | P-type and N-type | 2.5                   | 5.6                                    |
| a-Si RF plasma-enhanced chemical vapor deposition | boron doped p-type semiconductor | 3.9                   | 18                                      |
| CNTs Chemical vapor deposition | Single-layer and multi-layer | 0.17                  | 5.6 ~ 18                                |
| CNTs Novel spray coating and transfer technique | VO$_x$ coated multi-walled carbon nanotubes | 0.26                  | 2.8                                     |
| CNTs An MWNT decoration with almost full coverage by attaching ZnO nano-particles |Annealing at 400°C with insufficient oxygen titanium oxide-multi-walled carbon nanotube composite | 0.35                  | 7.5 x 10$^{-1}$                        |
| CNTs Boron doped P-type semiconductor | P-type and N-type | 0.41                  | 5.6                                     |
| CNTs An MWNT decoration with almost full coverage by attaching ZnO nano-particles | Suspension | 0.17                  | 5.6                                     |
| CNTs Sol-gel Annealing at 400°C with insufficient oxygen titanium oxide-multi-walled carbon nanotube composite | Suspension | 0.26                  | 5.6                                     |

References:
1. [5]
2. [7]
3. [11]
4. [12]
5. [13]
6. [15]
7. [16]
The thermally sensitive material absorbs the infrared radiation in the detector absorption layer. Part of the absorbed radiation power is dissipated by thermal radiation and heat conduction, and the other part is stored to increase the temperature of the thermal element. The heat transfer between the heating array and the air will lose heat, which is usually avoided by vacuum packaging. The final thermal balance is established between the temperature rise of the energy stored in the thermal array and the energy dissipated by heat conduction and infrared radiation.

Let the sensitive area of a pixel have a heat capacity of \( C \). Assume that the thermal conductivity of the primary heat loss mechanism, which is usually the thermal conductivity of the support structure, is \( G \). Time-modulated IR radiation with a power amplitude of \( \Phi_0 \) falls on the pixel. Let the fraction of incident absorbed radiation be \( \eta \). Let the angular modulation frequency of the radiation be \( \omega \). Let the temperature rise of the pixel-sensitive area be \( \Delta T \). When infrared radiation of an amplitude power of \( \Phi_0 \) sinusoidally modulated falls on the pixel with an angular frequency of \( \omega \), the temperature increase of the sensitive area of the pixel is \( \Delta T \). Then the heat flow equation describing the pixel is

\[
C \frac{dT}{dt} + GT = \eta \Phi_0 e^{i\omega t} 
\]

Then the steady-state solution of the heat flow equation is:

\[
\Delta T = \frac{\eta \Phi_0}{(G^2 + \omega^2 C^2)^{1/2}} 
\]

Obviously, under particular infrared radiation, when the \( \Delta T \) of the thermal element is higher, the detector’s material is more sensitive. With the modulation frequency \( \omega \) increasing, the heat capacity \( C \) is more significant than thermal conductivity \( G \). Then, we continue to increase the frequency, which will reduce \( \Delta T \). The parameter reflects the response time of the heat detector. \( \tau \) is the thermal response time, defined as

\[
\tau = \frac{C}{G} 
\]

Then the equation (1) can be expressed as follows:

\[
\Delta T = \frac{\varepsilon \Phi_0}{G(1 + \omega^2 + \tau^2)^{1/2}} 
\]

### 2.2. Bolometer performance parameters

The main performance parameters of the bolometer are voltage response rate (VR), noise equivalent power (NEP), and detection rate (D*). The temperature change of the bolometer causes the change of the physical quantity. The final measurement is usually the voltage signal, so the detector’s voltage response rate is its essential performance parameter. The bolometer’s voltage response rate is the ratio of its output voltage
signal (V) to the radiation power (P). It is generally expressed by
\[
\mathcal{R} = \frac{V}{P} = \frac{\eta_0 V_{\text{bias}}}{G \sqrt{1 + \omega^2 \tau^2}}
\]  

(5)

\(V_{\text{bias}}\) is the bias voltage.

The bolometer’s equivalent noise power is the output voltage generated by the infrared radiation projected on the bolometer precisely equal to the bolometer’s noise voltage. At this time, the radiation power of this infrared radiation is called the noise equivalent power.

\[
\text{NEP} = \frac{V_T}{\mathcal{R}}
\]  

(6)

\(V_T\) is the total noise voltage, described in detail in later chapters, \(\mathcal{R}\) is the voltage response rate.

In order to characterize the performance of detectors with different areas and noise bandwidths, the detection rate \(D^*\) is introduced. The detection rate is the signal-to-noise ratio obtained when the unit power radiation is irradiated on the sensitive element unit area under the amplifier’s unit bandwidth.

\[
D^* = \frac{A \Delta f}{\text{NEP}}
\]  

(7)

The unit of \(D^*\) is cmHz\(^{1/2}\)W\(^{-1}\).

2.3. Temperature coefficient of resistance

TCR is an essential parameter for measuring thermal sensitive materials, and its value is also related to the temperature environment. Most objects will change their resistance with the change of surrounding temperature [32]. Therefore, the TCR value of the thermal material can be calculated by measuring the resistance of the thermal material.

Assuming that the temperature increase \(\Delta T\) of the heat-sensitive materials due to the absorption of IR radiation is small enough so that the resistance change \(\Delta R\) is linear with \(\Delta T\), that is

\[
\Delta R = R \Delta T
\]  

(8)

So the parameter that indicates the relationship between material resistance and temperature is the TCR, which is defined as the relative rate of change of resistance with temperature, expressed by \(\alpha\).

\[
\Delta R = \alpha R \Delta T
\]  

(9)

Where

\[
\alpha = \frac{1}{R} \frac{dR}{dT}
\]  

(10)

It can be seen that when \(\alpha\) is larger, this means that the material is more sensitive to temperature. When the measured temperature reaches a certain temperature, the output signal of the detector will be large. Therefore, TCR is an important standard to measure the thermal properties of thermally sensitive materials.

All the heat-sensitive materials can be divided into three categories: metal, semiconductor, and superconductor. Moreover, TCR can be either positive or negative. For metals at room temperature, it is positive that the resistance increases with increasing temperature. It is called a positive temperature coefficient (PTC) heat sensitivity material. Common metal materials are nickel, bismuth, platinum, and antimony, generally used at low temperatures. Their typical \(\alpha\) is 0.03 -\%/K, and a specific detection rate is \(1 \times 10^6\) cmHz\(^{1/2}\)W\(^{-1}\) with a response time of about 10 ms. These materials are quite brittle at low temperatures, making it challenging to form arrays for imaging. The TCR is usually negative for semiconductors at room temperature, called a negative temperature coefficient (NTC). Most transition metal oxide semiconductors have an NTC. Among them, a class of semiconductor materials represented by vanadium oxide has a large NTC. A slight temperature rise within a specific temperature range will cause a resistance drop of 3 ~ 4 orders of magnitude. TiO\(_{2-x}\) is a kind of semiconductor material.

Superconductors include nickel-tin, lead-tin, NbN, etc, and their TCR is positive. In the phase transition temperature of the superconductor, the tiny temperature change will cause a significant change of resistance. Its detection rate can reach the order of microseconds or even nanoseconds. Therefore, the superconductor is a highly sensitive system. Superconducting materials need to work at a low temperature close to the temperature of liquid helium. The work temperature range is relatively narrow. With the further study of high-temperature superconducting materials of the YBaCuO system, superconducting bolometers working temperature has been developed rapidly. Phong et al [33] prepared the room temperature YBaCuO microbolometers with TCR value up to 4 -\%/K. And the optical responsivity and detectivity of the bolometers were \(7 \times 10^4\) V W\(^{-1}\) and \(3 \times 10^9\) cmHz\(^{1/2}\)W\(^{-1}\) at low frequencies, respectively.
The temperature dependence of the resistance is expressed as

\[ R(T) = R_0 \exp \left( \frac{E_a}{kT} \right) \]  

(Eq. 11)

\( E_a \) is the activation energy, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( R_0 \) is a constant.

With equations (10) and (11), the following equation can be obtained:

\[ \alpha = \frac{1}{R} \frac{dR}{dT} = -\frac{E_a}{kT^2} \]  

(Eq. 12)

2.4. Noise mechanism

There are many noises, including readout integrated circuit (ROIC) related noise, thermal fluctuation noise, Johnson noise, and Flicker (1/\( f \)) noise. Among them, Johnson noise and Flicker noise are electrical noise.

Thermal fluctuation noise is thermal noise mainly caused by fluctuations of heat exchange between the device and the environment. They are all random noise, and ultimately thermal noise will also be expressed in electrical signal fluctuations on the detector’s output signal.

2.4.1. Johnson noise

When the temperature is \( T \), the flux of the heat-sensitive material radiation is \( A \varepsilon \sigma T^3 \). Where \( A \) is the area, \( \varepsilon \) is the emissivity or absorption rate. When the temperature rises by a small \( dT \), the temperature is \( T + dT \) ignoring the higher-order term, \( \sigma \) is the Stefan-Boltzmann constant. The increment \( d\Phi \) of the radiant flux is \( 4A \varepsilon \sigma T^3 dT \) and the thermal conductivity \( G \) corresponding to this increment is

\[ G = \frac{d\Phi}{dT} = 4A \varepsilon \sigma T^3 \]  

(Eq. 13)

The mean square thermal fluctuation noise power of the heat exchange between the bolometer and the environment within the frequency bandwidth is

\[ \mathcal{P}_{\text{thermal}} = (4kT^2G) \Delta f = 16A \varepsilon \sigma T^5 \Delta f \]  

(Eq. 14)

The root mean square voltage is expressed as

\[ V_{\text{thermal}} = \mathcal{P} \sqrt{4kT^2G\Delta f} \]  

(Eq. 15)

Where \( \mathcal{P} \) is the response rate is the ratio between the output electrical signal and the input infrared signal. \( \Delta f \) is the thermal noise bandwidth, and \( G \) is the effective thermal conductivity.

Johnson noise is thermal noise, also known as Nyquist noise. It is caused by the carriers’ random movement inside the resistance device colliding with the lattice atoms, thereby showing the phenomenon that the voltage across the resistance fluctuates irregularly from the mean value. Its value is closely related to temperature. When the temperature rises, the carrier movement will intensify, and Johnson’s noise will also become more extensive. The root mean square voltage of Johnson noise is

\[ V_{\text{Johnson}} = \sqrt{4kTR\Delta f} \]  

(Eq. 16)

Here, \( k \) is the Boltzmann constant, \( T \) is the resistive device’s temperature, and \( \Delta f \) is the bandwidth. From the equation, we can conclude that the value of Johnson noise is not related to the detector’s bias voltage and frequency. It is a kind of ‘white noise’ whose value depends on the temperature \( T \) and the electronic bandwidth \( \Delta f \).

2.4.2. 1/\( f \) noise

1/\( f \) noise is also called flicker noise or modulation noise, which is a frequency-dependent noise. When the bolometer’s operating frequency is in the low-frequency range below 1 kHz, 1/\( f \) noise is relatively large. Moreover, when the operating frequency is greater than 1 kHz, it becomes a constant again. The generation of 1/\( f \) noise is closely related to the inherent defects of the crystal. The low-band noise with large noise is that the material of the photosensitive layer of the detector pixel is uniformly distributed. Alternatively, there are certain impurities and defects in the heat-sensitive materials of the bolometer. A micro-spark discharge occurs between the material particles when current flows through the bolometer, generating a micro-electric explosion pulse.

The following equation can define the voltage spectral noise density related to 1/\( f \) noise:

\[ S(f) = \frac{V_f^2}{f} = k \frac{V_{\text{bias}}^2}{f} \]  

(Eq. 17)

\( k \) is the 1/\( f \) noise parameter, strongly influenced by the bolometer materials, and \( V_{\text{bias}} \) is the bias voltage.
Of all the noise, thermal fluctuation noise is sufficiently low. Therefore, we only consider the Johnson and Flicker noise components as essential contributors to the bolometer’s performance. The Johnson noise measured under zero bias conditions has an almost constant power spectral density over the entire frequency, and the noise level is below 1/f noise so that it can be ignored. In general, 1/f is the dominant type of noise among the noises sources mentioned earlier. Because 1/f noise is low-frequency noise, which mainly depends on the materials, contact quality, and other factors, we can reduce the 1/f noise by improving the heat-sensitive material.

2.5. Universal bolometric parameter ($\beta$)

The universal bolometric parameter ($\beta$) is the ratio between the TCR ($\alpha$) value and the square root of the 1/f noise parameter ($k$). $\beta$ is an important parameter for evaluating the bolometer’s thermal materials, which are related to the TCR and 1/f noise. It is given by

$$\beta = \frac{|\alpha|}{\sqrt{K}}$$

Here,

$$K = \frac{\alpha\mu}{n} = \Omega \times k$$

(18)

Where $\alpha_{fi}$ is the Hooge parameter, $n$ is the charge carrier density, $K$ is the normalized Hooge parameter. $\Omega$ is the volume of the material. TCR, 1/f noise, and $\beta$ are considered essential evaluation indicators for thermal materials’ performance. Therefore, the research on heat-sensitive materials mainly focuses on reducing 1/f noise and improving TCR to improve the universal bolometric parameter ($\beta$).

3. Fabrication technologies

3.1. Structural design of bolometer

Many design features and tradeoffs should be considered to design an array of uncooled infrared bolometers with high sensitivity. Some of the most critical bolometer design parameters have been described in detail above, including high absorption rate of infrared radiation in a large area, bolometer temperature sensing material with a high TCR, low 1/f noise characteristics, and a sufficiently low thermal time constant of the bolometer. Furthermore, it is vital for commercial bolometer applications that the bolometer pixels are small enough. The reduction of the bolometer pixels would greatly increase the fill factor in a small area to reduce the cost and improve the focal plane array’s resolution. By reducing the effective size of the focal plane array (FPA), the cost of FPA chips and infrared optics can be decreased.

The key point of obtaining a high-performance bolometer is to design a thermal isolation structure with thermal conductivity. The micro-bridge structure has the advantages of small size, simple processing technology, and low thermal conductivity, making it the first candidate for thermal insulation structures. Micro-bridge structure can be divided into single-layer micro-bridge structure and double-layer micro-bridge structure.

3.2. Single-layer micro-bridge structure

The schematic diagram of a traditional single-layer bolometer micro-bridge structure is shown in figure 2. The micro-bridge structure comprises three parts: supporting bridge legs, bridge piers, and bridge deck, with the bridge legs and bridge deck in the same plane. The entire micro-bridge structure is suspended on the substrate using the surface sacrificial layer technology, where the readout circuit of the micrometer radiometer is integrated. The heat-sensitive film would be deposited on the bridge surface. The bridge surface absorbs the radiation when explored to infrared radiation and causes a temperature rise, which induces a change in the infrared-sensitive film. The electrical channel in the bridge leg transfers the electrical charge to the substrate’s readout circuit to detect infrared radiation.

The bridge legs’ main functions in the microbridge structure are providing mechanical support to the bridge deck, electrical channels to readout circuit, and thermal insulation to the microbridge structure. The bridge deck’s primary function is to absorb as much infrared radiation as possible to assure the entire microbridge obtains a higher temperature change. Therefore, to achieve high infrared detection performance of the microcalorimetry radiometer and ensure the bridge legs provide sufficient mechanical support for the bridge deck, the thermal insulation of the bridge legs should be improved as better as possible.

Once the bridge legs’ material is determined, increasing the length-to-width ratio of the bridge legs is the principal means to improve the thermal insulation of the bridge legs. On the other hand, the bridge deck area should be increased as much as possible to improve the infrared absorption capacity of the bridge deck.
Therefore we introduce the concept of micro-measured radiometer unit fill factor. The fill factor of a micro-radiometer is defined as the portion of the bolometer pixel area used to absorb the incident infrared. The higher the fill factor means, the stronger the infrared absorption capability of the device. The fill factor of the traditional single-layer infrared bolometer is usually between 60% and 70%.

To obtain higher thermal isolation and a larger fill factor in the same cell size, various shapes of micro-bridge legs are widely reported, including I-type bridge legs [34], L-type bridge legs, U-shaped bridge legs [35], and snake-shaped bridge legs [36], etc. The I-shaped is the most typical bridge leg shape, with two supporting bridge legs a simple I shape, as shown in figure 3(a). This design is useful in ensuring good thermal insulation.
performance and guaranteeing the fill factor of the bolometer. The L-shaped leg is an improved design, with two supporting L-shaped bridge legs. And double length-to-width ratio, as exhibited in figure 3(b), further improves the thermal isolation performance of the microbridge and the fill factor. The U-shaped leg’s length-to-width ratio is also about twice that of the L-shaped leg, as displayed in figure 3(c). Although the thermal insulation performance has not been improved compared to the L-shaped leg, the U-shaped leg can effectively reduce the bridge’s stress. The serpentine leg can be seen as a combination of multiple U-shaped legs. As shown in figure 3(d), this bridge leg structure would achieve very high thermal insulation performance, but its cell fill factor is reduced simultaneously.

### 3.3. Double-layer micro-bridge structure

To increase the bolometer pixel fill factor, a double-layer micro-bridge structure has been created. The double-layer micro-bridge structure can be divided into three forms: umbrella-shaped double-layer micro-bridge structure, eaves-shaped double-layer micro-bridge structure, and hidden bridge-type double-layer micro-bridge structure. The fill factor of the double-layers infrared bolometer is up to 90%.

A typical umbrella-shaped double-layer microbridge structure is shown in figure 4. The umbrella-shaped micro-bridge structure includes an umbrella-shaped absorption layer, an optical cavity, a heat-sensitive film, bridge legs, bridge piers, and a substrate with integrated readout circuits. The bridge legs design the electrical channels to connect the thermosensitive film and the substrate readout circuit. The umbrella-shaped absorption layer is at the top of the entire micro-bridge structure, which can effectively improve the microbolometer unit’s fill factor and enhance the infrared absorption rate of the device. The heat-sensitive film and the bridge legs are under the umbrella-shaped absorption layer. Besides, the dual optical cavity design plays an essential role in the optical resonant cavity by adjusting the height of a specific cavity, further improving the device’s responsiveness.

The second structure is the eaves-shaped double-layered micro-structure, which can also be regarded as building an eaves structure above the traditional single-layer micro-bridge structure to increase the device’s filling factor further and improve the infrared absorption capacity (figure 5). Moreover, there is ample space under the eaves structure to ensure the length-to-width ratio of the bridge legs and enhance the micro-bridge structure’s thermal insulation performance. Thus, the infrared response rate of the bolometer can be improved.

The effective utilization of infrared radiation can also be enhanced by increasing the infrared absorption rate of the microbridge structure. Resonant optical cavity (Fabry–Perot) structure is the most popular method for uncooled microbolometer to enhance the absorption rate of a specific waveband, designed according to the principle of multi-layer thin film interference filtering. The typical structure is shown in figure 6.

### 3.4. Manufacturing techniques of bolometer focal plane arrays

The most commonly used manufacturing approaches for uncooled infrared bolometer FPAs are bulk silicon micromachining and surface micromachining. As for bulk silicon micromachining, the chemical isotropic or anisotropic etching process is adopted in the etching solution to make micro-channels micro-cavities on the silicon substrate to suspend the micro-bridge structure. Figure 7 shows the substrate’s selective etching under the bolometer to achieve an excellent thermal insulation effect.

The bulk silicon process’ advantage is the compatibility with the CMOS process, which means the low cost of the bolometer. However, the disadvantage is the dependent shape of the cavity sidewall on the crystal plane, and
a considerable part of the substrate material needs to be consumed. Second, bulk silicon micromachining is more challenging to integrate with the integrated circuit (IC) process.

The surface micromachining process is another manufacturing technique shown in figure 8. It enables the entire utilization of the current IC process and the control of the microstructure at a certain level. The microbridge structure can be made without damaging the bottom readout circuit, which is very suitable for large-scale area array devices.

First, we form an electrical contact pad and a reflective layer on ROIC. Then the sacrificial layer is spin-coated, which is typically high-temperature stable polyimide. Moreover, the bottom membrane is deposited by magnetron sputtering or plasma-enhanced chemical vapor deposition process, and then the thermally sensitive material TiO$_{2-x}$ is deposited on the bottom film. After the passivation layer is formed, a photoresist is patterned to selectively remove the TiO$_{2-x}$ material of the microbridge’s connecting legs (figure 8(a)). Figure 8(b) displays the removal of the TiO$_{2-x}$ layer. Then a hole is etched in the sacrificial layer to form an electrical connection between the electrical contact pad and the micro-bridge structure (figures 8(c) and (d)). Afterward, the infrared absorption layer is deposited on the film, and the micro-bridge structure’s fabrication is completed (figure 8(e)), followed by the removal of the sacrificial layer to form a resonant cavity (figure 8(f)).
4. Preparation technology of titanium oxide

There are many ways to prepare TiO$_x$ films: sol-gel method, pulsed laser deposition (PLD), atomic layer deposition (ALD), electron beam evaporation (EBE), magnetron sputtering (MS), radiofrequency (RF), and direct current (DC) magnetron sputtering.

4.1. Sol-gel
The sol-gel method is an inexpensive and straightforward film preparation method. The necessary steps are as follows: firstly, organic metal compounds are synthesized into sol in a liquid phase at low temperature using inorganic materials or metal alcohols as precursors. The sol is then applied to the substrate using lifting, spin coating, spraying, brush coating, etc. Finally, after drying, sintering, fixing its gradient component, gel solidification, and heat treatment, the film is obtained to remove organic matter. The advantages are: the precursor can be purified firstly; the sol-gel process can be carried out at room temperature, the preparation equipment, the preparation process, the operation mode are relatively simple, and is not limited by the substrate shape and size, easy doping, so can be prepared in a large area of the film. The disadvantage is that the refractive index gradient, the size, and thickness of the prepared film are difficult to control, the process control requirements are high, the film is prone to cracking and bubbles \[41\].

4.2. Pulsed laser deposition
PLD is a method that bombards objects with a laser and then deposits the bombarded materials on different substrates to obtain the precipitates or films. The advantage is that it is easy to control the component, and the deposited film is utterly consistent with the component of the target material. The process parameters can be adjusted arbitrarily, and there is no limit to the type of target. The disadvantage is that the deposited film’s uniformity is low, and it cannot be deposited on a large area of the substrate, which also limits the application of PLD in the radiant heat and infrared focal plane \[42\].

4.3. Atomic layer deposition
ALD is a method that can deposit substances layer by layer on the substrate surface in the monatomic film. ALD is similar to ordinary chemical deposition. However, in the process of ALD, the chemical reaction of a new layer of atomic film is directly related to the previous layer. In this way, only one layer of atoms is deposited in each reaction. With the development of science and technology, more and more applications will be found in the near future. According to this technology’s reaction principle and characteristics, all kinds of different materials can be deposited. The deposited materials include metals, oxides, carbides (nitrogen, sulfur, silicon), various semiconductor materials and superconducting materials \[43\].

4.4. Electron beam evaporation
EBE is a physical vapor deposition method. It uses a high-energy electron beam to accurately bombard the target in the crucible, convert the kinetic energy of electrons into heat energy, melt them and deposit them on the
substance. A film with a compact structure and stable performance can be grown [44]. At the same time, the target has a small heating area, reduced heat radiation loss and high thermal efficiency. In addition, EBE coating is more suitable for single material coating because most composite films will decompose under high-energy electron bombardment [45].

4.5. Magnetron sputtering
MS is a kind of Physical Vapor Deposition (PVD). It is a physical vapor deposition method widely used in the preparation of titanium oxide films. The main sputtering methods are RF sputtering, ion beam sputtering and DC magnetron sputtering [46].

Usually, high-purity metal titanium is used as the target material, and the substrate can be glass, c-Si, SiO₂/Si, Maria glass, single sapphire crystal, etc. The sputtering surface was first washed with Ar⁺ on the substrate. The substrate is at an Angle of 30°~ 60° from the target. The substrate heating temperature is generally 300 °C ~ 550 °C, and the vacuum is about 10⁻³ Pa. The vacuum chamber is typically an inert gas, which can be obtained by changing the oxygen partial pressure and substrate temperature to get titanium oxide films with different structures and performances [22].

The thickness of the film prepared by magnetron sputtering is easy to grasp, and the thickness of the film can be controlled within the required range in the process of preparation. The working current controls the deposition rate of vacuum sputtering coating. As long as the working current is strictly controlled, the die-making deposition rate can be well controlled, and the film thickness can be controlled. The film prepared by the magnetron sputtering method has good repeatability. At the same time, almost all solids can be prepared by sputtering, such as metal film, alloy film, dielectric film, oxide film, and semiconductor film, insulator film. As long as the target can be made, the film can be prepared. In addition, compound films can be prepared by reactive sputtering from elemental targets [47, 48].

5. TiO₂₋ₓ films for bolometer

5.1. The structure and property of TiO₂₋ₓ films
In general, the TiO₂₋ₓ films prepared at room temperature has no prominent diffraction peak on the x-ray diffraction pattern, which means that the TiO₂₋ₓ films are an amorphous structure at room temperature. Therefore, the composition and microstructure of the TiO₂₋ₓ films usually depend on the preparation conditions (figure 9(a)). For example, the oxygen partial pressure variation affects the composition of the material, and high reaction temperature usually induces an orderly structure of the film.

TiO₂₋ₓ has a wide bandgap (3.2 eV for anatase, 3.0 eV for rutile). Mardare et al [49] have researched the temperature dependences of the electrical conductivity and pointed out that when the temperature is high above 300 K, the measured conductivity of the TiO₂₋ₓ films can be explained by a simple thermal activation conduction mechanism. However, the conductivity occurs by variable range hopping (VRH) of carriers between local states at a low temperature below 300 K. Moreover, the activation energy of the hopping is much smaller than the simple activation conduction. The electron transport mechanism in the a-TiO₂₋ₓ obeys the Meyer-Neldel Rule (MNR). The MNR is an empirical relation that the pre-exponential factor of TiO₂₋ₓ films shows an exponential dependence as functions of the activation energies (figure 9(b)).

The equation is

\[ \ln \sigma_s = \ln \sigma_{s0} + \frac{E_a}{E_{MN}} \]  \hspace{1cm} (19)

Where \( \sigma_{s0} \) is Meyer-Neldel’s pre-exponential factor, \( E_{MN} \) is characteristic energy. And they are all constants.

5.2. The effect of preparation conditions for TiO₂₋ₓ

5.2.1. Deposition temperature
Deposition temperature is a vital deposition parameter that influences the bolometric properties of TiO₂₋ₓ films. The deposition rate of the film decreases with increasing temperature. When the sputtering temperature gradually increases, the deposition kinetic energy of the sputtered particles on the film surface becomes more massive, and the diffusion ability is much more potent. Therefore, the particles are tricky to deposit on the substrate and induce a relatively low deposition rate and thin film.

We can conclude from table 2 that TCR and activation energy (\( E_a \)) decreased with the increase of deposition temperature from 25 °C to 200 °C due to increased resistivity. The sample deposited at 200 °C has a low TCR but low \( 1/f \) noise parameter, indicating better bolometer performance of the TiO₂₋ₓ film deposited at 200 °C.
Table 2. The bolometric properties of TiO$_2$–$x$ films at different deposition temperatures. © 2013 IEEE. Reprinted, with permission, from [32].

| Sample (T$x$) | Dep. rate (nm min$^{-1}$) | Resistivity ($\Omega$·cm) | TCR (–%/K) | $E_a$ (eV) | $1/f$ noise parameter | $\beta (\times 10^{13})$ |
|--------------|--------------------------|--------------------------|------------|-----------|----------------------|-------------------|
| RT (25 °C)   | 5.1                      | 0.82                     | 2.54       | 0.19      | 3.16 × 10$^{-12}$    | 9.51              |
| 100 °C       | 4.63                     | 0.27                     | 2.36       | 0.18      | 1.60 × 10$^{-12}$    | 12.9              |
| 150 °C       | 4.47                     | 0.19                     | 2.25       | 0.17      | 7.97 × 10$^{-13}$    | 17.8              |
| 200 °C       | 4.07                     | 0.14                     | 2.09       | 0.16      | 3.35 × 10$^{-13}$    | 26.6              |
| 250 °C       | 3.32                     | 0.36                     | 2.18       | 0.17      | 1.23 × 10$^{-12}$    | 16.1              |

5.2.2. The oxygen pressure and thermal annealing

Annealing is a means of metal heat treatment process that mainly heats the metal slowly to a specific temperature for a sufficient time and then cools at a reasonable rate [50]. Thermal annealing of TiO$_2$–$x$ films is mainly to refine the grain and improve the structure of the films. The pressure of oxygen affects the trivalent titanium (Ti$^{3+}$) to tetravalent titanium (Ti$^{4+}$) in the TiO$_2$–$x$ films; as the oxygen pressure (pO$_2$) increases, the content of Ti$^{3+}$ decreases because of the deducing of the oxygen vacancies. There are many oxygen vacancies in the TiO$_2$–$x$ films obtained by magnetron sputtering. The films are unstable in the air and easy to oxidize after annealing treatment. The oxygen vacancy in TiO$_2$–$x$ film can be compensated. The structure and electrical properties of TiO$_2$–$x$ films deposited at different annealing temperatures will change significantly. Therefore, many orders of magnitude can be changed by changing titanium oxide films’ resistance and temperature coefficient [8].

TiO$_2$–$x$ films were deposited by RF reactive magnetron sputtering on Si/SiO$_2$ substrates with a 4 inch. Pure titanium (99.99%) targets at different relative mass flow of oxygen gas (RO$_2$) levels (3.4% ~ 3.7%) in mixed gas (Ar + O$_2$) atmospheres [8]. Oxygen and argon were used as the reactive and sputter gases, respectively, and these were adjusted discretely by mass flow controllers. At room temperature, the deposition process was performed in 18 min with a process pressure of 2 mTorr and an RF power of 300 W. The samples’ thickness varied from 90.1, 89.4, 88.9, to 69.8 nm by increasing the RO$_2$ from 3.4, 3.5, 3.6, and 3.7%, respectively [8]. To improve the performance of the bolometer, the sample is annealed at 300 °C in the atmosphere.

The effect of pO$_2$ on the surface morphology of TiO$_2$–$x$ films was observed through field emission scanning electron microscope (FESEM) images. Figure 10(a) shows that the deposited film has dispersed grains at lower pO$_2$. The surface of TiO$_2$–$x$ films becomes dense and smooth with the increase of pO$_2$. This may be due to the lower surface mobility of the particles deposited at higher pO$_2$. The deposited film was air annealed at 300 °C for one hour, as shown in figure 10(b). At lower pO$_2$, the annealed films show refined grains. However, the films exhibit a relatively dense and smooth surface with no grain characteristics at higher pO$_2$.

Figure 11 shows the X-ray diffraction and Raman spectra of the TiO$_2$–$x$ film sample after deposition and annealing. In figure 11(a), the deposited sample appears amorphous due to insufficient heat energy on the sample substrate. The annealed sample changes from amorphous to crystalline (rutile/anatase) [8]. In figure 11(b), no TiO$_2$–$x$ bands were observed in the deposited samples, indicating that they had an amorphous structure, while the annealed samples showed anatase/rutile TiO$_2$–$x$ bands [51].

Due to the oxygen vacancy decrease, the bandgap increases with the RO$_2$ level, which leads to the number of defect states decreasing near the edge of the conduction band (figures 12(a) and (b)). The decrease of
bandgap in annealed samples may be due to the decrease of atomic spacing and crystallinity change \[52\]. It can be seen that annealing might reduce the material’s bandgap because the crystallinity will increase when the atomic distance is reduced \[53\].

As shown in table 3, TCR increases with the RO\(_2\) because the oxygen vacancy can be offset with ascending RO\(_2\) and the electron concentration will be reduced \[54\]. The TCR of annealed samples is slightly lower than that of as-deposited samples except for the samples with higher RO\(_2\) parameters.

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Figure 10. FESEM images of (a) as-deposited and (b) 300 °C annealed TiO\(_2\) films at various oxygen partial pressures. Reprinted from [22]. Copyright (2015), with permission from Elsevier.

Figure 11. X-ray diffraction and Raman spectroscopy of the TiO\(_2\) film sample after deposition and annealing. Reprinted from [8], with the permission of AIP Publishing.
Annealed samples show lower $1/f$ noise parameters than deposited samples, as concluded from figures 12(c) and (d). Samples with higher RO2 parameters show higher resistivity, lower carrier density, and higher activation energy. Samples with high resistance usually have higher noise, while samples with low resistivity are more suitable for better device performance because $1/f$ noise is dominant at low frequency and depends on temperature, contact quality, surface treatment, and carrier density [55].

XRD and Raman results show that TiO$_2$–x film exhibits better crystallinity, narrower bandgap and lower resistivity after annealing. It can be seen that the TiO$_2$–x after thermal annealing has the advantages of low resistivity, low $1/f$ noise, and high thermal radiation parameters, etc, which can ensure effective thermal radiation measurement performance.

### 5.2.3. Nb doping

During the preparation process of TiO$_2$–x films, titanium is very sensitive to oxygen. Even if the amount of pO$_2$ in the reaction chamber changes slightly, the resistivity of the TiO2–x film will change greatly [23]. The flow of oxygen in the reaction chamber should be carefully controlled to obtain certain film resistivity. It is a challenge to
ensure high accuracy in this process. In order to control the TiO$_2$–$x$ film’s resistivity, the researchers tried to incorporate Nb metal atoms into the TiO$_2$–$x$ film. Nb atoms act as an extrinsic donor in the TiO$_2$–$x$ films whose Nb$^{5+}$ state replaces the Ti$^{4+}$ state due to their similar ionic radii, which can reduce the oxygen sensitivity and resistivity of the material [56, 57].

Before each deposition step, the target is pre-sputtered in an Ar environment for 15 min to remove the oxide layer or any other possible surface contamination. In a mixed gas atmosphere, Nb-doped titanium is used as a metal target, and a doped titanium oxide film is prepared on a 4-inch SiO$_2$/Si substrate using RF reactive magnetron sputtering technology. The target was placed in the sputtering chamber at a distance of 140 mm from the substrate at an inclination of 45°. The pressure in the sputtering chamber is kept below 3 × 10$^{-7}$ Torr. The film was deposited at room temperature at a constant RF power of 300 W for 14 min. When the total flow rate is 50 sccm, the O$_2$/(O$_2$ + Ar) ratio of the main combustion chamber varies from 4.3% to 4.8% [25].

When pO$_2$ reaches 4.7%, the TiO$_2$–$x$ film shows a stable state. The deposition rate decreased significantly when pO$_2$ ascended up to 4.8%. When the titanium target’s reaction rate with oxygen is greater than the sputtering rate, the target’s surface is completely oxidized, and the construction mode changes from the metal mode to the oxide mode [25]. A metal peak of titanium is observed in figure 13(a) when the pO$_2$ content is 4.3%.

Whereas no rutile and anatase crystal structure when the pO$_2$ level is higher than 4.3% due to enough oxygen reacting with titanium atoms. The resistivity and TCR of Nb-doped TiO$_2$–$x$ films are 0.05 Ω cm and 1.88 × K$^{-1}$, which are lower than those of other films [25]. The resistivity of Nb-doped and pure TiO$_2$–$x$ samples varies from 0.39 to 2.48, and 0.82 to 42.65, respectively, with the increase of pO$_2$. The resistivity of Nb-doped TiO$_2$–$x$ films is much lower than that of pure TiO$_2$–$x$ films due to the decrease of oxygen vacancies and the decrease of carrier concentration with the increase of pO$_2$ level, which leads to the increase of resistivity [58]. The Nb concentration in Nb-doped TiO$_2$–$x$ films does not change with the pO$_2$ level, so the resistivity does not increase significantly.

As shown in figure 13(b), as the number of oxygen vacancies decreases, the carrier jump’s activation energy increases. Compared with a pure titanium oxide film, doped niobium TiO$_2$–$x$ film has a higher TCR value.

The voltage density of 1/f noise is in the test range of 1 ~ 1000 Hz. As displayed in figure 13(c), the thin film’s resistivity has a significant influence on the value of the 1/f noise parameter. When Nb doping reduces the TiO$_2$–$x$ film’s resistivity, a lower 1/f noise parameter can be obtained.

The XRD results show that the amorphous phase is formed when the content of pO$_2$ is between 4.4% and 4.7%. XPS analysis confirms that the increase of resistivity is due to increased pO$_2$ and the decrease of oxygen vacancies. The resistivity of Nb-doped TiO$_2$–$x$ films decreases significantly. Nb-doped TiO$_2$–$x$ films have lower resistivity, lower 1/f noise parameter, higher TCR value, and better radiation calorimetry characteristics.

5.2.4. Thermal stability of Nb–TiO$_2$–$x$

Infrared equipment will encounter a high-temperature environment in use. In a high-temperature environment, the infrared detector will appear ghost image phenomenon to reduce the burn effect at high temperatures. Franken et al [59] reduced the resistance variation characteristics of a VO$_2$–based uncooled microbolometer simple with annealing treatment. They annealed the samples at a high current to remove the ghost image, but the resistivity of annealed samples decreased. Therefore, increasing the current for annealing is not a fundamental solution to the ghost image [60].

TiO$_2$–$x$ has made significant progress in device manufacturing and thermal metering performance [8, 23, 61]. TiO$_2$–$x$ is highly sensitive to oxygen, and the oxygen vacancy in TiO$_2$–$x$ during preparation makes the resistivity challenging to be adjusted. To effectively control the resistivity of TiO$_2$–$x$, Nb doping in TiO$_2$–$x$ is a common way to regulate electrical properties [62, 63].
Niobium ions were replaced by Ti lattice to reduce the number of oxygen vacancies. High-temperature annealing was carried out in an oxygen environment to reduce the oxygen vacancy in Nb: TiO$_2$$_{\text{-}x}$ [32, 64]. Oxygen atoms could diffuse into the film at high temperatures and occupy oxygen vacancies [65–67]. The diffusion mechanism of oxygen during annealing in the oxygen atmosphere is exhibited in figure 14(a). It is clearly shown that oxygen vacancies are offset by oxygen atoms diffusion during high-temperature annealing [60].

Figure 14(b) shows the XRD patterns of the as-deposited and annealed samples. No prominent diffraction peak proves an amorphous structure of the as-deposited film. Clear polycrystalline (101) and (200) orientations of the rutile TiO$_2$$_{\text{-}x}$ phase were observed for the film annealed in an oxygen atmosphere. There are no Nb$_2$O$_5$ peaks in the XRD image, indicating that Nb was dissolved entirely in TiO$_2$$_{\text{-}x}$ during deposition. The radii of Nb$^{5+}$ and Ti$^{4+}$ ions are 70 pm and 68 pm, respectively, indicating that Nb$^{5+}$ ions can easily occupy the position of Ti lattice and form a stable, reliable solution.

As shown in figure 14(c), the sample deposited at room temperature does not show the Raman spectra of TiO$_2$$_{\text{-}x}$, indicating that the film is amorphous. In the annealed sample, the Raman spectra of 230 cm$^{-1}$ (broadband), 436 cm$^{-1}$ (E$_g$), and 614 cm$^{-1}$ (A$_1$g) are observed, which correspond to rutile structure [68, 69].

The firm photoelectron peaks of Ti, O$_2$, and Nb can be seen in figure 15(a). As shown in figure 15(b), each sub-peaks relative area concentration in the backward sample decreases with the reduction of oxygen vacancy. The ratio of O$_2$ to O$_3$ in the samples after annealing decreases slightly, as proved in figure 15(c), indicating that the concentration of oxygen vacancy decreases after annealing in the oxygen atmosphere [70]. The O$_5$ spectrum’s relative peak area in the annealed sample increases slightly, which indicates that oxygen atoms can diffuse into the film after annealing and reduce the oxygen vacancy concentration [71]. No additional peak was observed in figure 15(d) at the lower binding energy of Nb 3d$_{5/2}$.

As shown in table 5, Ti and Nb atom percentages decrease, O$_2$ atom percentage increases, and O$_2$/(Ti+Nb) increases in annealed samples. Combined with the XPS diagram, it can be concluded that annealing at high temperatures ($450$ °C) can compensate for oxygen vacancy.

When annealed in an oxygen-rich environment, external oxygen atoms diffuse into the film and occupy the oxygen vacancy. Besides, thermal stability tests at different exposure temperatures show that the samples with
less oxygen vacancy have higher thermal stability. Although the annealed samples’ thermal metrology performance decreased slightly, the thermal stability was significantly improved compared with the deposited samples. This type of oxygen vacancy compensation method opens a new opportunity to enhance titanium oxide films’ thermal stability and other oxide materials annealed in an oxygen atmosphere [60].

5.2.5. Atomic layer deposition
ALD is a deposition technique separated by intermittent evacuation or purification when different precursors are introduced. This method has a high advantage because of its limited growth. This makes it possible to deposit a large area of uniform film with single-layer thickness and control the single layer’s thickness. The nanofilm prepared by ALD has good thermal conductivity and near-ideal optical properties, which greatly improves the bolometer [72].

At present, there are few ways to characterize TiO$_2$–$x$ films by TCR, which are mainly formed by RF reactive magnetron sputtering and DC sputtering deposition [26]. Kwon et al [29] studied reactive sputtering TiO$_2$–$x$ thin films and obtained TCR values up to 2.8–%K Reddy et al [8, 23] grew TiO$_2$–$x$ films under the same conditions.

Table 4. Chemical compositions of the as-deposited and annealed TNO samples. Reproduced from [60]. © IOP Publishing Ltd. All rights reserved.

| Sample            | Atomic% (±0.1) | O/(Ti + Nb) (±0.1) |
|-------------------|----------------|--------------------|
|                   | Ti  | Nb | O   |                  |
| As-deposited      | 36.01 | 0.35 | 63.64 | 1.75              |
| O$_2$-annealed    | 33.25 | 0.30 | 66.45 | 1.98              |
deposition technique but different oxygen content, the TCR value was 3.66 −% /K. Jiang et al reported the TCR of TiO$_2$ thin film prepared by reactive DC sputtering method was 3.3 −% /K [50]. The substrate was fixed to the deposition chamber after cleaning, and ALD treatment was started. Due to the low deposition temperature, it is necessary to extend the cleaning time to improve the films’ quality. Tetrakis(dimethylamino)titanium (IV) (TDMAT) was used as the reaction precursor of titanium, and milli-Q water (H$_2$O) was used as the reaction precursor of oxygen. The TDMAT precursor was kept at 75 °C, and the TDMAT pulse, N$_2$, H$_2$O, and N$_2$ pulse of 100 ms, 1 min, 15 ms, and 1 min were carried out within a cycle, respectively. The deposition rate of TiO$_2$ film is 0.4 Å /cycle. N$_2$ was used as the carrier gas with a flow of 20 sccm. The samples were deposited at temperatures of 150, 200, and 250 °C, respectively, and then annealed at different temperatures (300, 330, 475, 550 and 600 °C) based on Thermogravimetric Analysis (TGA), and annealed in a conventional furnace in the air for 1 h [26].

TCR measurements use temperature control during the healing phase, where the temperature varies between 15 °C and 40 °C, while the voltage on the resistor is recorded by applying a current of 1 to 10 μA. Noise measurements are made by applying a 3 μA current to the resistor and measuring the resistor’s voltage with the help of an amplifier and a dynamic signal analyzer. After the measurement, the noise power spectral density of the resistance is obtained, and the angular noise frequency of 1 / f noise is calculated [26].

Figure 16(a) shows the grazing incident X-ray diffraction pattern of the deposited TiO$_2$ film annealed at different temperatures. It can be deduced from figure 16(a) that the as-deposited TiO$_2$ film is amorphous, and anatase occurs when the temperature rises above 300 °C. Both the strength of anatase and the crystallinity of thin-film increase with the annealing temperature. It is found that the thin film annealed at 600 °C has low-intensity diffraction of the rutile phase. According to TGA and XPS analysis, the phase transition from anatase to rutile appears to occur at 475 °C. Hanaro et al [73] report that the initial transition temperature from anatase thermal activation to rutile depends on experimental parameters such as deposition method, deposition temperature, and different substrates [26].

Figure 16(b) shows the XPS measurement scanning spectra of TiO$_2$ annealed at different temperatures. C1s spectrum exists at 285 eV, which is used as the standard reference line. Ti 2p and O 1s are adjusted according to this energy. For the combination of O-H and O-Ti, the O1s spectrum consists of two peaks, which are associated with 530 and 531.6 eV, respectively. Figure 16(c) shows the high-resolution O1s spectrum. The two peaks of the O-Ti and O-H bonding states were used to match the O1s spectrum [74–77]. The O/Ti ratio first increases and then decreases with the increase of temperature. At 475 °C, the O/Ti ratio reached the highest, which was 1.84.

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**Table 5. Resistivity values of TiO$_2$−x film based on coating/annealing temperatures. Reproduced from [26], with the permission of the American Vacuum Society.**

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

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**Figure 16.** (a) X-ray diffraction patterns of TiO$_2$−x films annealed at various temperatures. A, anatase phase; R, rutile phase. (b) Broad scan survey x-ray photoelectron spectra of TiO$_2$−x films annealed at various temperatures. (c) Detailed O1s analysis of TiO$_2$−x films as-deposited and annealed at various temperatures. Reproduced from [26], with the permission of the American Vacuum Society.
As shown in table 5, the crystal structure is more orderly, reducing the oxygen vacancy and the resistivity after annealing. It can be seen that the temperature of the coating has little influence on resistivity.

As shown in figure 17(a), the thin film’s resistance changed significantly with growth temperature. The results show that the TCR value of the film is strongly dependent on the temperature angular frequencies of the TiO$_{2-x}$ films annealed at 300 and 475 °C are 1.8 and 1.2 k Hz, respectively, which are consistent with the angular frequencies of most microbolometer materials, as shown in figure 17(b). Due to the increase of crystallinity and the decrease of defects, the value of cracker noise is lower at higher annealing temperatures [26].

As shown in table 6, the maximum TCR values of TiO$_{2-x}$ films are between 20 and 30 °C and TCR value at 25 °C based on coating/annealing temperatures. Reproduced from [26], with the permission of the American Vacuum Society.

| Coating/annealing temperature(℃) | TCR value at 25℃ (%/K) | Maximum TCR value between 20 and 30℃ (%/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                                      |

As shown in table 5, the crystal structure is more orderly, reducing the oxygen vacancy and the resistivity after annealing. It can be seen that the temperature of the coating has little influence on resistivity.

As shown in figure 17(a), the thin film’s resistance changed significantly with growth temperature. The results show that the TCR value of the film is strongly dependent on the temperature angular frequencies of the TiO$_{2-x}$ films annealed at 300 and 475 °C are 1.8 and 1.2 k Hz, respectively, which are consistent with the angular frequencies of most microbolometer materials, as shown in figure 17(b). Due to the increase of crystallinity and the decrease of defects, the value of cracker noise is lower at higher annealing temperatures [26].

As shown in table 6, the maximum TCR values of TiO$_{2-x}$ films are between 20 and 30 °C. By controlling the annealing temperature, a higher TCR value can be obtained. The samples annealed at low temperature (300 °C and 330 °C) have mixed phases (anatase and rutile), which can produce metastable films, while the samples are annealed at high temperature (475 °C and above) change with the annealing temperature. The results show that the highest TCR value of the TiO$_2$ film grown at 150 °C and annealed at 300 °C is 9 -%/K, which is much higher than that of the active layer used in commercial microbolometers [26].

In summary, compared with the films without annealing, the TCR values of the films coated and annealed at different temperatures are higher (9 -%/K), and the results of the electrical noise test also verify that annealing is a feasible method to improve the properties of the films [26].

5.2.6. Microwave plasma etching

At present, the preparation methods of dense, uniform and high-quality films have been developed very maturely whether one or more film optimization methods can quickly process the prepared TiO$_{2-x}$ film so that the resistance of the prepared titanium oxide film changes and the TCR value increases. Qiming et al [78] prepared 300 nm titanium oxide thin films by EBE. EBE method is conducive to the evaporation of high melting point materials. Due to the high flux density produced by electron beam heating, the evaporation rate can be improved to a certain extent. Microwave plasma etching (MPE) technology interacts with atoms on the crystal surface and active atoms under high voltage and low power RF. The 300 nm thick TiO$_{2-x}$ films were etched by microwave plasma for $2 \sim 6$ min in an oxygen and argon atmosphere. Through research and analysis, the
resistance of titanium oxide film after 4 min of MPE shows a linearly decreasing trend, and its TCR value increases from 0.32429 %/K to 1.65751 %/K [78].

Figure 18. (a) XRD analysis of TiO$_{2-x}$ under different MPE times. (b) Raman spectra of TiO$_{2-x}$ under different MPE times. Reproduced with permission from [78].

In Figure 18(a), the diffraction peaks at 25.281$^\circ$ and 27.446$^\circ$ correspond to the diffraction peaks of anatase (101) and rutile (110) of TiO$_{2-x}$. In figure 18(b), three Raman peaks appear at 144 cm$^{-1}$, 448 cm$^{-1}$ and 608 cm$^{-1}$, and these three Raman peaks become obvious with the time of MPE. The results show that the crystal form of TiO$_{2-x}$ film after MPE changes from amorphous to crystalline, and the crystal quality is also improved [78].

In Figures 19(a) and (c), the obvious binding energy peaks of Ti at 464.3 ± 0.2 eV and 458.5 ± 0.2 eV correspond to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ orbits, respectively [74, 79]. After MPE for 4 min, the peak value of Ti$^{3+}$ increased relatively. In Figures 19(b) and (d), the peak value of Os decreased significantly in the TiO$_{2-x}$ film.

Figure 19. XPS analysis fitting diagram. (a) TiO$_{2-x}$ element in Ti films prepared by EBE. (b) TiO$_{2-x}$ element in O films prepared by EBE. (c) TiO$_{2-x}$ element in Ti film after MPE for 4 min (d) TiO$_{2-x}$ element in O film after MPE for 4 min. Reproduced with permission from [78].
With the increase of Ti$^{3+}$ peak and the decrease of Os peak, it can be concluded that there is oxygen vacancy in TiO$_2$–$x$ film [59, 78].

We can see from figure 20 that with the increase of MPE time, the surface of TiO$_2$–$x$ film is rough due to the impact of microwave plasma. At the same time, hydrogen, as a reaction gas, may react with oxygen in the film [78]. With the increase of temperature, the resistance of the films decreased, which can confirm that MPE can change the conductivity of TiO$_2$–$x$ film. There is a strictly linear relationship between the resistance and temperature of TiO$_2$–$x$ film treated by MPE for 4 and 5 min, which is conducive to the characteristics of bolometer applications. The temperature dependence of the resistance of 4 min TiO$_2$–$x$ film is greater than that...
Table 7. Preparation and optimization of TiO$_2$–x film.

| Materials | Preparation methods | Optimization methods | TCR (%/K) | 1/f noise parameter (V$^2$ Hz$^{-1}$) | $\beta$ ($\times 10^{13}$/K m$^{-3/2}$) | References |
|-----------|---------------------|----------------------|-----------|----------------------------------------|----------------------------------------|------------|
| TiO$_2$–x | RF reactive magnetron sputtering | Deposition temperature 200 °C | 2.09 | 3.16 $\times 10^{-12}$ | 26.6 | [32] |
| TiO$_2$–x | RF reactive magnetron sputtering | Annealing at 300 °C for 1 h at room temperature | 2.26 | 1.21 $\times 10^{-13}$ | 43.37 | [8] |
| Nb:TiO$_2$–x | RF reactive magnetron sputtering | 1 atomic % of niobium (Nb)-doped titanium (Ti) (99.99%) metal target. | 3.1 | — | — | [25] |
| Nb:TiO$_2$–x | RF reactive magnetron sputtering | 1 atomic % of niobium (Nb)-doped titanium (Ti) (99.99%) metal target. 75 °C to 100 °C deposition | 2.38 | 2.4 $\times 10^{-13}$ | 29 | [60] |
| Nb:TiO$_2$–x | RF reactive magnetron sputtering | 1 atomic % of niobium (Nb)-doped titanium (Ti) (99.99%) metal target. Annealing at 450 °C for 30 min in an oxygen environment | 2.43 | 1.02 $\times 10^{-13}$ | 14.41 | [60] |
| TiO$_2$–x | ALD | ALD at 150 °C and annealing at 300 °C | 9 | — | — | [26] |
| TiO$_2$–x | EBE | Microwave plasma etching in hydrogen and argon atmosphere for 4 min | 1.65751 | — | — | [78] |
of 5 min film, and the thermal sensitivity is better. The TCR value of TiO$_{2-x}$ film after MPE for 4 min is calculated to be 1.65751-%/K \[78\], as shown in figure 21.

The TiO$_{2-x}$ film was prepared by EBE and optimized by MPE. XRD, Raman, XPS, SEM and other analysis methods were used to characterize, and it was concluded that MPE could effectively change the characteristics of TiO$_{2-x}$ film. Finally, preparation and optimization of TiO$_{2-x}$ film were given out in table 7.

**6. Summary and conclusion**

This paper has discussed the bolometer’s main performance parameters and manufacturing technology, which can inspire us to design a bolometer with better performance. We also explored the application of TiO$_{2-x}$ films for bolometers and summarized the methods for improving the bolometric properties of TiO$_{2-x}$ films material at home and abroad.

TiO$_{2-x}$ material is a promising candidate for heat-sensitive materials on a bolometer. To achieve the bolometer’s high performance, we have investigated the effect of the deposition process on the film structure, composition, and electrical properties of this material, such as resistivity, TCR, and activation energy. Furthermore, these factors are very crucial for the detectivity of thermal IR detectors. The TCR of TiO$_{2-x}$ film can move up to 3.6-%/K with a relatively low 1/f noise parameter. Titanium oxide-based 12 μm pixel pitch uncooled bolometer has been made and shown better-infrared imaging performance.

The performance and resolution of the bolometer have improved significantly in the past five years. The bolometer’s performance is getting closer to the theoretical limit, and the distance from the photon detector is getting smaller. The bolometer has advantages in terms of weight, power consumption, and cost of non-refrigeration technology. Therefore, its output is more extensive than all other infrared array technologies. Radiometer arrays have become the technology of choice for low-cost infrared imaging systems used in civilian and military applications. The future development must be a bolometer with smaller pixels. Simultaneously, titanium oxide material has good thermal stability, and the advantages of compatibility with the CMOS process will be the focus of bolometer material research.

Through the elaboration of this paper, it can be explained that TiO$_{2-x}$ film can be effectively used as the heat sensitive material of bolometer, and it has good heat sensitive properties. In the future, researchers may be able to select thermal materials according to external factors such as application scenarios and temperature range. At the same time, taking appropriate preparation methods, exploring appropriate experimental parameters through experiments, and exploring effective film optimization methods under the condition of ensuring the uniformity and quality of the film will be the way to promote the application research of TiO$_{2-x}$ as a bolometer. The bolometer using TiO$_{2-x}$ film as thermal sensitive material has good compatibility with CMOS. TiO$_{2-x}$ has various phases in nature, and its oxygen content can be changed flexibly by external force. TiO$_{2-x}$ has stable chemical properties, non-toxic and good photocatalytic activity. Therefore, TiO$_{2-x}$ can be used as thermistor material for more exploration.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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