

## Article

# Thermoelectrical Properties of ITO/Pt, In<sub>2</sub>O<sub>3</sub>/Pt and ITO/In<sub>2</sub>O<sub>3</sub> Thermocouples Prepared with Magnetron Sputtering

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**Abstract:** ITO/Pt, In<sub>2</sub>O<sub>3</sub>/Pt and ITO/In<sub>2</sub>O<sub>3</sub> thermocouples were prepared by the radio frequency (RF) magnetron sputtering method. The XRD results showed that all the annealed ITO and In<sub>2</sub>O<sub>3</sub> films annealed at high temperature present a cubic structure. Scanning electron microscope results showed that the thickness of the ITO and In<sub>2</sub>O<sub>3</sub> films could reach 1.25 μm and 1.21 μm, respectively. The ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thin film thermocouples could obtain an output voltage of 68.7 mV and 183.5 mV, respectively, under a 900 °C temperature difference, and at the same time, the Seebeck coefficient reached 76.1 μV/°C and 203.9 μV/°C, respectively. For the ITO/In<sub>2</sub>O<sub>3</sub> thermocouple, the maximum value of the output voltage was 165.7 mV under a 1200 °C temperature difference, and the Seebeck coefficient was 138.1 μV/°C. Annealing under different atmosphere conditions under 1000 °C, including vacuum, air and nitrogen atmospheres, resulted in values of the Seebeck coefficient that were 138.2 μV/°C, 135.5 μV/°C and 115.7 μV/°C, respectively.

**Keywords:** ITO thin film; In<sub>2</sub>O<sub>3</sub> thin film; thermocouples; magnetron sputtering



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## 1. Introduction

With the continuous progress and development of the aviation industry, the performance of the engine, which is the core device of the aviation industry, is required to be more and more efficient, which requires the aero-engine to work stably in an extreme environment for a long time [1–3]. At the same time, the distribution of the temperature field inside the engine and the temperature value of high-temperature components are also necessary information in the process of engine design and improvement. Because it is easy to cause irreparable damage to the internal structural components of the engine under high-temperature conditions, it is necessary to control the internal temperature to avoid the erosion and other damage of the internal components caused by high temperature. [4] The high-temperature test of the aeroengine mainly includes the measurement of the internal combustion chamber wall, combustion chamber inlet and outlet gas, turbine blade surface, tail nozzle and other high-temperature components of the engine to obtain the temperature and distribution of these components. The data obtained from these tests are of great significance to the design and development of the engine [5]. Two kinds of measurement are performed for high-temperature components: contact and non-contact. The non-contact type uses the radiation signal issued by the measured components for measurement, such as infrared spectrum measurement [6,7] and the optical fiber method of measurement [8]. Contact measurement involves installing the temperature-sensing device on the surface of the component or integrated in the component, through the change of material characteristics or thermoelectric effect measurement. These methods include the crystal method [9–11], temperature paint method [12,13], and thermocouple method [14].

Thermoelectric tests can be conducted in two ways: standard armor and thin film thermocouple. The small thin film thermocouple can be easily integrated on the surface of

the high-temperature components and convert the thermal signal into an electrical signal, so that the real-time temperature value of the measured components can be obtained. In addition, the thickness of the thin film thermocouple is generally only in the order of micrometers, which can be ignored on the structure of the components. Further, it has the advantages of fast response, small thermal capacity and impact resistance [15,16], so it has therefore attracted considerable attention in the measurement of high-temperature components. There are many ways to prepare thin film thermocouples. Physical vapor deposition can be used on the surface of components, such as RF magnetron sputtering, DC sputtering, evaporation coating, etc. [17]. The application of thin film thermocouples to the testing of high-temperature engine components is suitable for the measurement of special extreme environments, such as the acquisition of the temperature parameters of engine turbine blades, combustion chamber walls and outlets, and provides accurate and reliable experimental data for design and improvement. Therefore, the design of thin film thermocouples and their application to high-temperature measurements have important practical significance.

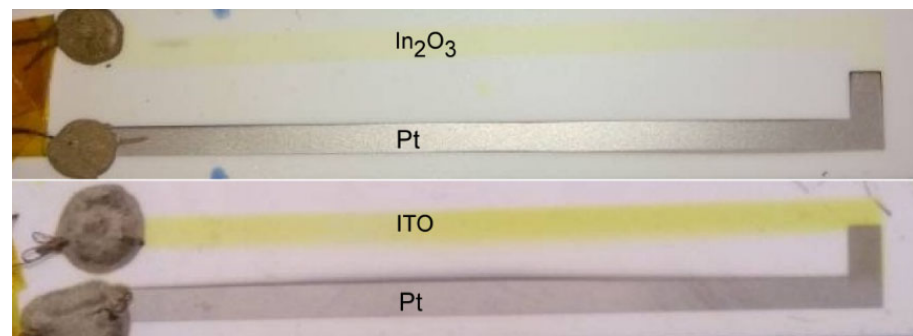
With precious metal thin film thermocouples, such as Pt, Rh, WRe and other materials [18–20], the maximum measurable temperature is relatively low, and they are prone to failure conditions, such as falling off, oxidation, and large errors in extreme environments of high temperature, strong gas flow and strong corrosion. In addition, the Seebeck coefficient of precious metal thin film materials is small, resulting in small output voltage values. Therefore, it is necessary to select materials with better performance to replace noble metal materials as the electrodes of thin film thermocouples [21,22]. In order to solve many problems encountered by metals and their alloy materials in high-temperature engines, such as low resistance to high temperature, weak adhesion with the substrate, easy to fall off and easy to oxidize at high temperatures, oxide semiconductor materials have been selected because of the advantages of high-temperature resistance, corrosion resistance, oxidation resistance, etc. Moreover, their Seebeck coefficient is far greater than that of metal thin film materials, so they have also become an important direction for the selection of thin film thermocouple electrode materials [23–25]. With ITO/Pt thin film thermocouples on nickel-based substrates using alumina as insulating [26], the maximum test temperature can reach 1100 °C, the output value can reach about 50 mV, and the Seebeck coefficient can reach about 45  $\mu\text{V}/^\circ\text{C}$ .

In this study, ITO ( $\text{In}_2\text{O}_3$ , 10 wt%  $\text{SnO}_2$ ),  $\text{In}_2\text{O}_3$  and Pt films were successfully deposited on an alumina surface; the metal mask was used to form an electrode pattern; and the ITO/Pt,  $\text{In}_2\text{O}_3$ /Pt and ITO/ $\text{In}_2\text{O}_3$  thermocouples were finally constructed. Laboratory tests were conducted to determine the properties of the thin film thermocouples. The microstructure of each of the ITO and  $\text{In}_2\text{O}_3$  films was characterized in detail with an X-ray diffraction meter and scanning electron microscope. Moreover, the thermoelectrical performances of the ITO/Pt,  $\text{In}_2\text{O}_3$ /Pt and ITO/ $\text{In}_2\text{O}_3$  thermocouples were systematically characterized.

## 2. Materials and Methods

ITO/Pt,  $\text{In}_2\text{O}_3$ /Pt and ITO/ $\text{In}_2\text{O}_3$  thermocouples were deposited with the RF magnetron sputtering system (JPG-560, Sky Technology Development co., LTD., Shenyang, China). Figure 1 shows photographs of the ITO/Pt and  $\text{In}_2\text{O}_3$ /Pt samples. The ITO,  $\text{In}_2\text{O}_3$  and Pt electrodes were 3 mm wide and 9.5 cm long, and the size of the substrates was 2 cm  $\times$  10 cm with a 1 mm thickness. The overlap area between the three kinds of electrodes on the hot junction area was about 3 mm  $\times$  3 mm.  $\text{Al}_2\text{O}_3$  substrate with single-sided polishing was selected for the experiment, and ultrasonic cleaning was used to remove organic and inorganic substances on the surface of the silicon wafer. The cleaning process steps were as follows. The  $\text{Al}_2\text{O}_3$  substrate was put into the culture dish, we added a proper amount of alcohol and acetone in turn, and each ultrasonic cleaning time was 10 min. After cleaning, the  $\text{Al}_2\text{O}_3$  substrates were washed with deionized water, then dried with  $\text{N}_2$ , and were put into a drying oven at 100 °C for 30 min. After cleaning, the metal mask was placed on

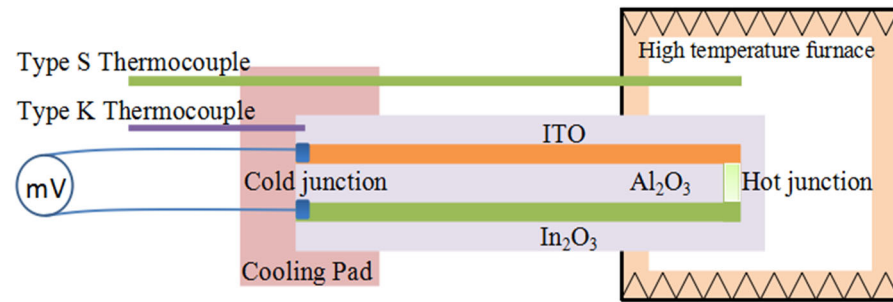
the surface of the alumina substrate, and the ITO or  $\text{In}_2\text{O}_3$  electrode pattern was formed on the surface of the substrate through the sputtering process. The diameter of the ITO and  $\text{In}_2\text{O}_3$  target was 4 inches, and the sputtering parameters of the ITO and  $\text{In}_2\text{O}_3$  films are as follows: the sputtering pressure was 2.0 Pa, the sputtering power was 100 W, the argon–oxygen ratio was 9:1, the sputtering time was 7 h. Then, all the ITO and  $\text{In}_2\text{O}_3$  films were annealed at 1000 °C in a tubular furnace under an air atmosphere for 60 min. In order to characterize the effects of the annealing atmosphere on the performance of the thermocouple, three different atmosphere conditions of vacuum, air and nitrogen were used in the entire heat treatment of the prepared ITO/ $\text{In}_2\text{O}_3$  thermocouple samples. A tubular furnace (OTF-1200, Kejing Materials Technology Co., LTD., Hefei, China) was used for heat treatment equipment. Under the condition of the vacuum atmosphere, the vacuum value was  $6.0 \times 10^{-1}$  Pa, and the heat treatment temperature was 1000 °C for 60 min.



**Figure 1.** Physical images of ITO/Pt and  $\text{In}_2\text{O}_3$ /Pt samples.

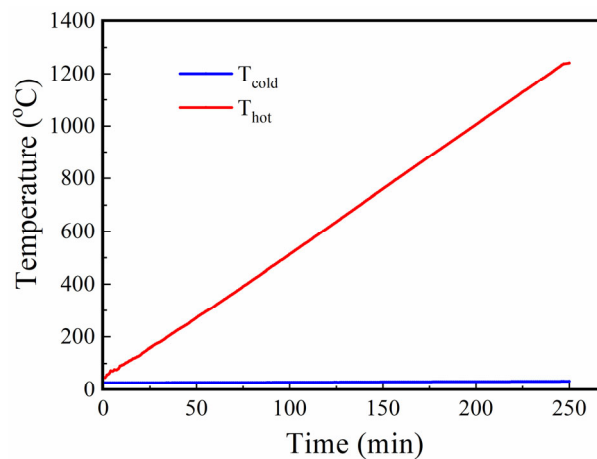
After the ITO and  $\text{In}_2\text{O}_3$  films were deposited on the  $\text{Al}_2\text{O}_3$  substrate and annealed, another Pt electrode of the thermocouple was prepared by magnetron sputtering, and it formed a partial overlap area with the ITO or  $\text{In}_2\text{O}_3$  electrode at the hot end. The Pt target with a diameter of 4 inches, thickness of 4 mm, sputtering pressure of 0.5 Pa, sputtering power of 100 W, and argon flow of 80 sccm was selected, and the sputtering time was 40 min. Before depositing the Pt film, the metal mask was placed on the surface of the alumina to form a Pt electrode. Enamelled copper wire was used to connect the cold end of the thermocouple sample. The length of the copper wire was 20 cm, and the diameter was 0.5 mm. Silver paste was used as the adhesive, and the sample was dried at 150 °C for 30 min to ensure a good ohmic contact between the copper wire and the ITO and  $\text{In}_2\text{O}_3$  films. The output voltage value of the system was measured and recorded by a data recorder (LR8431, HIOKI, Shangtian City, Japan), which can simultaneously record the voltage or temperature curve of 10 channels, and the voltage accuracy can reach 5  $\mu\text{V}$ .

The structures of each ITO and  $\text{In}_2\text{O}_3$  film sample were characterized with an X-ray diffraction meter (XRD, D/max-2400, Rigaku, Tokyo, Japan). The surface and cross-sectional SEM images were obtained with a field-emission scanning electron microscope (FESEM, Quanta 250 FEG, FEI, Portland, OR, USA). As Figure 2 illustrates, the test system consisted of the heating part, voltage acquisition, temperature acquisition at the hot and cold ends of the thermocouple, and a cooling unit. The heating unit was a high-temperature heating furnace (LHT 2-17, Nabertherm, Bremen, Germany). For the temperature measurement at the connection point of the hot end of the thermocouple, a WRP-100 standard S-armored thermocouple was used for testing the hot end of the thermocouple. The measurement range was in the range from room temperature to 1250 °C. Between the hot and cold ends, alumina foam transfer and high-temperature asbestos material were used for the insulation treatment, and the thermocouple sample was passed through the alumina foam brick to ensure a significant temperature difference between the two ends of the thermocouple, so as to obtain an accurate output voltage value. For the cold end of the thermocouple, the standard K-type thermocouple was used to measure the temperature of the cold junction.



**Figure 2.** Schematic of ITO/ $\text{In}_2\text{O}_3$  thermocouple test set-up.

Figure 3 illustrates the temperature change trends at the cold and hot ends of the thermocouples used in the experiment. During the heating process, the heating rate was set at  $5\text{ }^\circ\text{C}/\text{min}$ . During the entire heating process, the temperature at the cold end changed very little and remained at a lower temperature. Using the data recorder to obtain the temperature of the cold and hot ends at the same time, the temperature difference between the cold and hot ends of the thermocouple can be calculated. With the temperature difference as the abscissa, the thermal voltage of the thermocouple samples and the Seebeck coefficient as the ordinate, the change relationship curve of the output thermoelectric voltage, Seebeck coefficient and temperature difference of the thermocouple samples can be obtained.

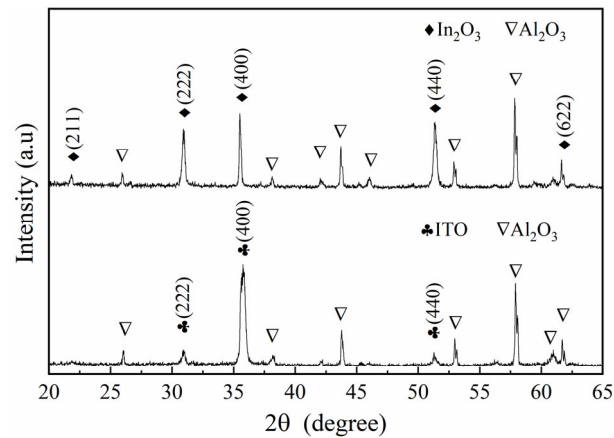


**Figure 3.** Temperature change curve of thermocouple cold and hot ends.

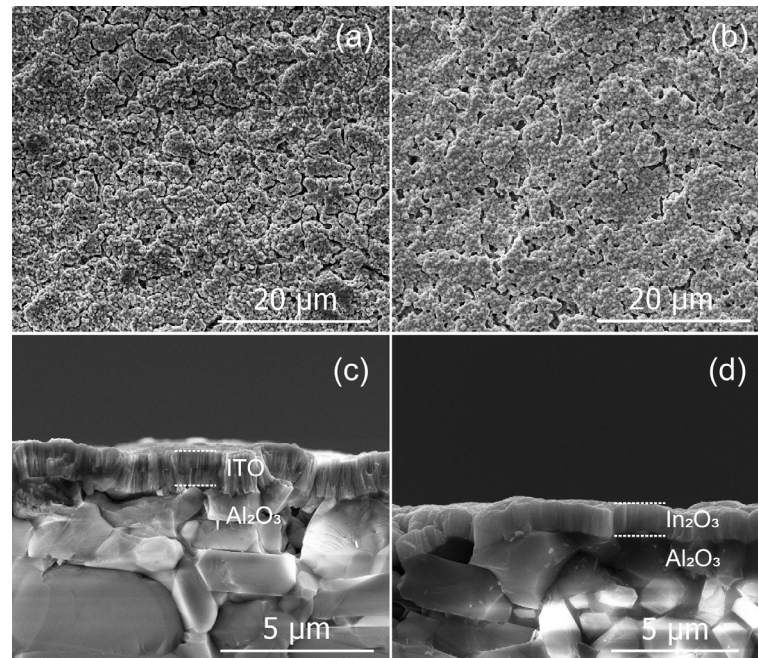
### 3. Results

#### 3.1. Microstructure of ITO and $\text{In}_2\text{O}_3$ Thin Films

Figure 4 shows the XRD diffraction patterns of the ITO and  $\text{In}_2\text{O}_3$  thin films after the heat treatment in the air atmosphere. It can be seen from the XRD diffraction results that the ITO and  $\text{In}_2\text{O}_3$  films present a cubic structure, in which no characteristic diffraction peak of  $\text{SnO}_2$  is observed, indicating that Sn atoms have entered the  $\text{In}_2\text{O}_3$  structure to form a stable solid melt. After annealing, the (222), (400) and (440) peak strengths of the ITO and  $\text{In}_2\text{O}_3$  films are obvious. Figure 5 shows the surface morphology and cross-section of the ITO and  $\text{In}_2\text{O}_3$  films. After annealing at  $1000\text{ }^\circ\text{C}$  for 1 h, visible grains can be observed on the surface of the ITO and  $\text{In}_2\text{O}_3$  films in Figure 5a,b. As there are no obvious cracks on the film surface, the rough film surface must have been caused by the high roughness of the alumina substrate. Figure 5c,d display the obvious fault structure of the ITO and  $\text{In}_2\text{O}_3$  films, and the thickness of the ITO and  $\text{In}_2\text{O}_3$  films could reach  $1.25\text{ }\mu\text{m}$  and  $1.21\text{ }\mu\text{m}$ , respectively.



**Figure 4.** XRD patterns of ITO and  $\text{In}_2\text{O}_3$  thin films.



**Figure 5.** Surface morphology and cross-section of ITO film and  $\text{In}_2\text{O}_3$  film: (a) ITO surface image; (b)  $\text{In}_2\text{O}_3$  surface image; (c) ITO cross-section; (d)  $\text{In}_2\text{O}_3$  cross-section.

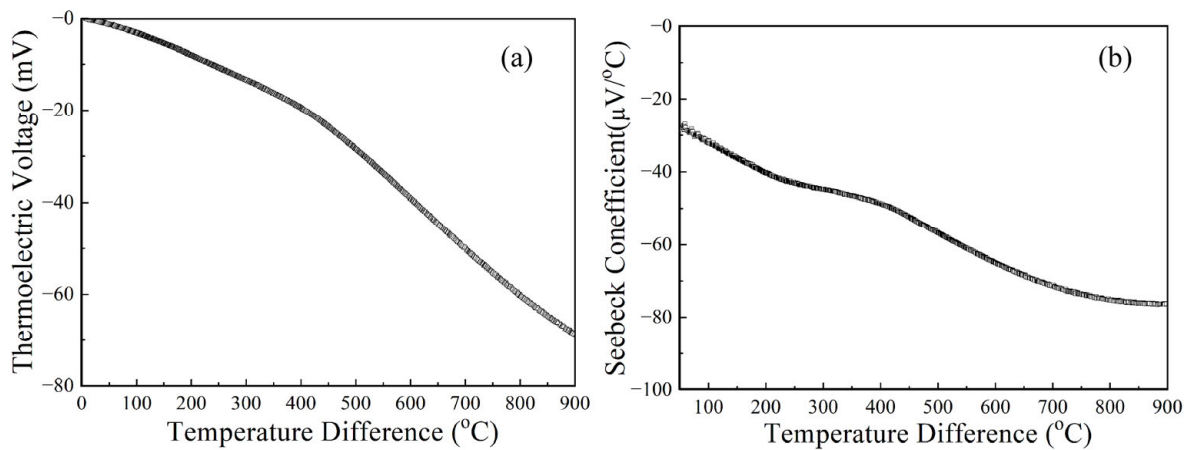
### 3.2. Thermoelectrical Properties of ITO/Pt and $\text{In}_2\text{O}_3$ /Pt

Figure 6a illustrates the relationship between the output thermal voltage of the ITO/Pt thin film thermocouple and the temperature difference between the cold and hot ends of the thermocouple. To prevent Pt electrode failure, the maximum temperature of the hot end was set at about  $950\text{ }^\circ\text{C}$ . As can be seen from Figure 6a, when the temperature difference between the cold and hot ends of the thermocouple reached  $900\text{ }^\circ\text{C}$ , the absolute value of its output voltage was  $68.7\text{ mV}$ . Because ITO is an n-type semiconductor, its output was negative. Figure 6b shows that the Seebeck coefficient varied with the temperature. The Seebeck coefficient of the thermocouple increased linearly as the temperature difference increased. When the temperature difference between the cold and hot ends of the thermocouple reached  $900\text{ }^\circ\text{C}$ , the Seebeck coefficient was  $76.1\text{ } \mu\text{V}/^\circ\text{C}$ . It can be seen from the figure that the Seebeck coefficient of the ITO/Pt basically maintained a linear increasing trend in the low temperature section with the increase of the temperature. In the high-temperature section, especially when the temperature difference was close to  $900\text{ }^\circ\text{C}$ , the Seebeck coefficient showed a trend of slowing down. This phenomenon was caused by the interaction between the phonons and electrons in the material. According to the Kubakaddi

model, the Seebeck coefficient is composed of two parts: the sum of the components caused by electron diffusion and the components caused by phonon drag [27,28]:

$$S = S_d + S_g = \frac{2k}{e} - \frac{k}{e} \ln \left[ \left( \frac{2\pi}{m^*kT} \right)^{\frac{1}{2}} \hbar n a^2 \right] \quad (1)$$

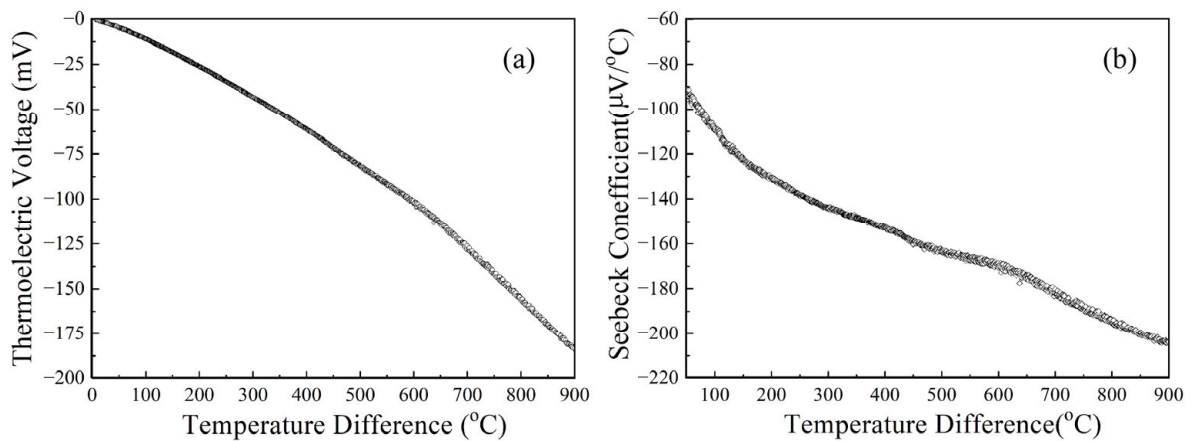
where  $S$  is the Seebeck coefficient,  $n$  is the carrier concentration,  $k$  is the Boltzmann constant,  $\hbar$  is the Planck's constant,  $e$  is the electron charge,  $a$  is the transverse dimension, and  $S_d$  is the Seebeck coefficient component due to diffusion, while  $S_g$  is the Seebeck coefficient component due to phonon drag.



**Figure 6.** Thermoelectric response curve of ITO/Pt thermocouple. (a) Thermal voltage output; (b) Seebeck coefficient.

At the low-temperature stage, the electron diffusion component played a leading role, with a weak interaction between the phonons and electrons, so the Seebeck coefficient was relatively small. As the temperature rose, the interaction between the phonons and electrons became stronger. In the direction of the temperature gradient, along the direction of the thermocouple from the hot end to the cold end, the drag of the phonons on the electrons became more and more obvious, and the drag component of the phonons became stronger. Therefore, the Seebeck coefficient increased continuously and exhibited a linear-increase trend. With a further temperature increase at the hot end of the thermocouple, in the direction of the temperature gradient, the interaction among phonons played a leading role, and its drag on the electron became weaker. This inhibited the movement of the electron along the direction of the temperature gradient, slowing down the output of the ITO/Pt thin film thermocouple at high temperatures.

Figure 7a shows the relationship between the output thermal voltage of an  $\text{In}_2\text{O}_3/\text{Pt}$  thermocouple and the temperature difference between the hot and cold ends. When the temperature difference reached 900 °C, the absolute value of the output voltage was 183.5 mV. Figure 7b shows how the Seebeck coefficient varied with the temperature. The Seebeck coefficient of the thermocouple increased as the temperature difference increased. When the temperature difference between the hot and cold ends of the thermocouple reached 900 °C, the value of the Seebeck coefficient was 203.9  $\mu\text{V}/^\circ\text{C}$ . The Seebeck coefficient of the  $\text{In}_2\text{O}_3/\text{Pt}$  thermocouple also showed the same change trend. The drag effect of the phonons on electrons was greater at the cold end, and the rate of increase was faster, whereas at the hot end, the rate slowed down because of the interaction among the phonons.



**Figure 7.** Thermoelectric response curve of In<sub>2</sub>O<sub>3</sub>/Pt thermocouple. (a) Thermal voltage output; (b) Seebeck coefficient.

For the output curves of the ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thermocouples, a cubic polynomials, namely, that expressed in Equation (2), was used to fit the results [29]:

$$E = A(\Delta T)^3 + B(\Delta T)^2 + C(\Delta T) + D \quad (2)$$

where  $E$  is the output thermal voltage of the ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thermocouples;  $\Delta T$  is the value of the difference in the temperature between the cold and hot ends of the thermocouple;  $A$ ,  $B$ ,  $C$  and  $D$  are the coefficients of each part of the polynomial. The coefficient  $D$  is set to zero during fitting, because the output thermal voltage should be zero when the temperature difference between the cold and hot ends is zero, and the output thermal voltage output should be zero. The fitting results of the heating curve of the ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thermocouples are shown in Table 1, where the average Seebeck coefficient represents the average value of all the Seebeck coefficients of the thermocouples during all the heating stages and represents the fitting degree. As can be seen, the fitting degree of the two heating curves of the ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thermocouples was greater than 99.9%. According to the output thermal voltage value of ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt, the output thermal voltage value of the ITO/In<sub>2</sub>O<sub>3</sub> thermocouple can be deduced, and it should be the difference between the absolute values of the ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thermocouples. The average Seebeck coefficient of the ITO/In<sub>2</sub>O<sub>3</sub> thermocouple can also be deduced, and it was approximately 127.8  $\mu\text{V}/^\circ\text{C}$ .

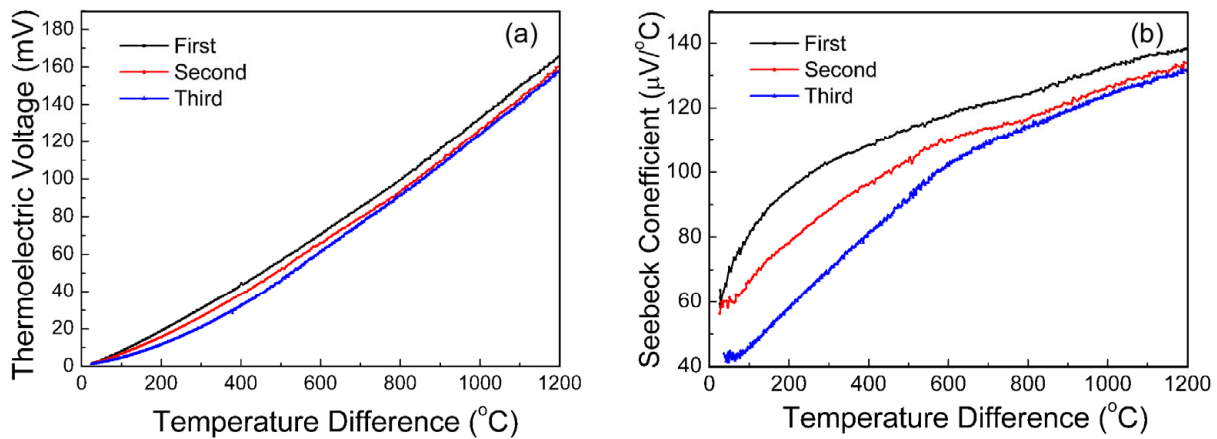
**Table 1.** Polynomial fitting results of ITO/Pt and In<sub>2</sub>O<sub>3</sub>/Pt thin film thermocouples.

Type	A (mV/°C <sup>2</sup> )	B (mV/°C)	C (mV)	D	R <sup>2</sup>	Seebeck Coefficient at 900 °C Difference (µV/°C)
ITO/Pt	$3.592 \times 10^{-8}$	$-1.001 \times 10^{-6}$	-0.017	0	0.9995	76.1
In <sub>2</sub> O <sub>3</sub> /Pt	$-1.339 \times 10^{-8}$	$-8.967 \times 10^{-5}$	-0.113	0	0.9998	203.9

### 3.3. Thermoelectrical Properties of ITO/In<sub>2</sub>O<sub>3</sub>

To characterize the output characteristics of the ITO/In<sub>2</sub>O<sub>3</sub> thin film thermocouple, three calibration experiments were conducted calibrating the thermocouple with a thermocouple test system. As the results presented in Figure 8a illustrate, the output voltage of the ITO/In<sub>2</sub>O<sub>3</sub> film thermocouple increased linearly with the increasing of the temperature. When the temperature difference between the cold and hot ends was 1200 °C, the temperature of the hot end was 1256 °C. The output of the thermocouple could reach 165.7 mV. The Seebeck coefficient of the thermocouple during three calibrations is shown in Figure 8b. When the temperature difference between the hot and cold ends was 1200 °C,

the maximum value of the Seebeck coefficient could reach  $138.1 \mu\text{V}/^\circ\text{C}$ . In addition, during the entire heating process, the Seebeck coefficient in the cubic calibration curve increased continuously with the rising of the temperature, and the rate of increase was faster in the low-temperature section, but slowed down in the high-temperature section. This was because the drag between the phonons and electrons in the low-temperature section was obvious, while the interaction among the phonons in the high-temperature section played a dominant role [30–32].



**Figure 8.** Output calibration and Seebeck coefficient change of  $\text{In}_2\text{O}_3/\text{ITO}$  thermocouple. (a) Thermal voltage output; (b) Seebeck coefficient.

In the calibration curve results of the third calibration experiment, the output value of the thermocouple also changed. This resulted from the hot end heating at a high temperature and the microstructure change of the film after heating. As can be seen, the calibration curves of the second and third experiments were closer, indicating that the performance of the thermocouple was stable. Table 2 shows the polynomial fitting results of the cubic calibration curves of the thermocouple. It can be seen that the values of all the calibrated curves were greater than 99.9%. In addition, the Seebeck coefficient of the entire heating process reached  $138.1 \mu\text{V}/^\circ\text{C}$ , which was higher than that of  $\text{ITO}/\text{Pt}$  ( $76.1 \mu\text{V}/^\circ\text{C}$ ) and lower than that of  $\text{In}_2\text{O}_3/\text{Pt}$  ( $203.9 \mu\text{V}/^\circ\text{C}$ ).

**Table 2.** Fitting results of output calibration polynomial of  $\text{ITO}/\text{In}_2\text{O}_3$  thin film thermocouple.

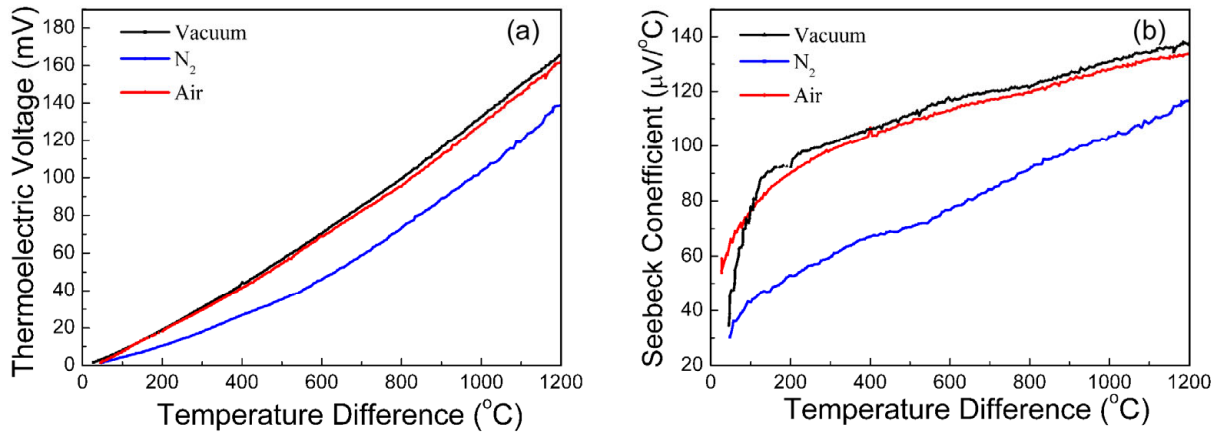
Type	A ( $\text{mV}/^\circ\text{C}^2$ )	B ( $\text{mV}/^\circ\text{C}$ )	C (mV)	D	R <sup>2</sup>	Seebeck Coefficient at 1200 °C Difference ( $\mu\text{V}/^\circ\text{C}$ )
First	$-1.609 \times 10^{-8}$	$6.249 \times 10^{-5}$	0.084	0	0.9996	138.1
Second	$-2.064 \times 10^{-8}$	$7.959 \times 10^{-5}$	0.067	0	0.9992	134.2
Third	$-4.824 \times 10^{-8}$	$1.384 \times 10^{-5}$	0.034	0	0.9993	132.3

### 3.4. Effect of Annealing Atmosphere on Thermoelectric Properties

Figure 9a shows the thermoelectric output curves under different heat treatment atmospheres. The thermocouple samples prepared were heat treated under the three different conditions of vacuum, air and nitrogen. The heat treatment was conducted within a tubular furnace. For nitrogen heat treatment, the gas flow meter was adjusted to maintain the flow of  $\text{N}_2$  at 50 sccm. The output voltage of the heat treatment under the  $\text{N}_2$  atmosphere and vacuum conditions was lower than that of the heat treatment samples under the air condition during the entire heating process, especially under the  $\text{N}_2$  atmosphere. The output curves showed good linearity under the three conditions. When the temperature difference between the hot and cold ends of the thermocouple was  $1200^\circ\text{C}$ , the output of the thermocouple under the air, vacuum and  $\text{N}_2$  atmospheres was 165.9 mV,



162.6 mV and 138.9 mV, respectively. The trend of the Seebeck coefficient variation trend of the thermocouple under the different heat treatment conditions is shown in Figure 9b. The Seebeck coefficient also increased in the duration of the heating process. When the temperature difference was 1200 °C, the Seebeck coefficients under the vacuum, air and N<sub>2</sub> atmospheres were 138.2 μV/°C, 135.5 μV/°C and 115.7 μV/°C, respectively.



**Figure 9.** Thermoelectric output curve and Seebeck coefficient change of In<sub>2</sub>O<sub>3</sub>/ITO thermocouple under different atmospheres. (a) Thermal voltage output; (b) Seebeck coefficient.

Table 3 shows the polynomial fitting results of the curves of the thermocouple under the different heat treatment conditions. The maximum output value of the thermocouple was obtained under the vacuum heat treatment. This was because the thermoelectric output performance of ITO and In<sub>2</sub>O<sub>3</sub> varied under the different heat treatment atmosphere conditions. The Seebeck coefficient of ITO and In<sub>2</sub>O<sub>3</sub> can be expressed by Equations (3) and (4), respectively [33].

$$S(N_D) = -\left(\frac{\pi}{3N_D}\right)^{2/3} \frac{8\kappa^2 m^* T}{3e\hbar^2} \left(A + \frac{3}{2}\right) \quad (3)$$

$$S(N_D) = -\frac{Ak}{e} - \frac{k}{e} \ln\left(\frac{(2\pi m_e^* KT)^{2/3}}{\hbar^3 N_D}\right) \quad (4)$$

where  $S$  is the Seebeck coefficient,  $N_D$  is the carrier concentration,  $\kappa$  is the Boltzmann constant,  $\hbar$  is the Planck's constant,  $e$  is the electronic charge,  $m^*$  is the Electronic effective mass,  $A$  is the transmission coefficient.

**Table 3.** Fitting results of output calibration polynomial of In<sub>2</sub>O<sub>3</sub>/ITO thin film thermocouple.

Type	A (mV/°C <sup>2</sup> )	B (mV/°C)	C (mV)	D	R <sup>2</sup>	Seebeck Coefficient at 1200 °C Difference (μV/°C)
Vacuum	$-1.609 \times 10^{-8}$	$6.429 \times 10^{-5}$	0.084	0	0.9999	138.2
Air	$-9.978 \times 10^{-8}$	$5.557 \times 10^{-5}$	0.083	0	0.9999	135.5
N <sub>2</sub>	$-1.109 \times 10^{-8}$	$6.542 \times 10^{-5}$	0.039	0	0.9999	115.7

The output thermal voltage and the Seebeck coefficient of the overall sensor depend on the changes in the thermoelectric properties of the two electrode materials. After annealing in different heat treatment conditions, the output characteristics of the ITO/In<sub>2</sub>O<sub>3</sub> thermocouples have changed. Under the same temperature difference at the cold and hot ends, the sample output value after the heat treatment in the N<sub>2</sub> gas atmosphere was the smallest, caused by N atoms entering the ITO and In<sub>2</sub>O<sub>3</sub> thin film structure during high-temperature heat treatment. For ITO, N atoms entering the structure occupied the oxygen

vacancy generated in the sputtering process, which reduced the carrier concentration. The entry of an N atom bonded two free electrons in the film structure, which decreased the concentration of free electrons in the ITO film and increased the Seebeck coefficient of the film electrode. The case of the  $\text{In}_2\text{O}_3$  thin film was different; it was a non-degenerate semiconductor, and when N atoms entered the film structure, the N atoms acted as a valence band acceptor, which led to the reduction of the output thermoelectric potential of  $\text{In}_2\text{O}_3$  [32]. Under the influence of these factors, the overall output of the thin film thermocouple treated with the  $\text{N}_2$  atmosphere showed a significant downward trend. For the thermocouple samples treated in a vacuum and air at high temperatures, the oxygen vacancy in the thin film electrode decreased after the high temperature in the air atmosphere. Therefore, in the thermoelectric output results, the output value of the sample treated in an air atmosphere was slightly lower than that of the sample treated in a vacuum, which also made the Seebeck coefficient slightly lower when the temperature difference was  $1200^\circ\text{C}$ .

#### 4. Conclusions

ITO/Pt,  $\text{In}_2\text{O}_3$ /Pt and ITO/ $\text{In}_2\text{O}_3$  thin film thermocouples were prepared on an  $\text{Al}_2\text{O}_3$  substrate by using the radio frequency magnetron sputtering method. The microstructure of the ITO and  $\text{In}_2\text{O}_3$  thin films was investigated, and all the ITO and  $\text{In}_2\text{O}_3$  thin films have a cubic structure, and the annealed film has a relatively dense surface structure. The section structure shows that all the films are continuous without fracture, and the films have a thickness of more than  $1.2\ \mu\text{m}$ . At a  $900^\circ\text{C}$  temperature difference, the output of the ITO/Pt and  $\text{In}_2\text{O}_3$ /Pt thermocouples reached  $68.7\ \text{mV}$  and  $183.5\ \text{mV}$ , respectively, and the maximum of the Seebeck coefficient was  $76.1\ \mu\text{V}/^\circ\text{C}$  and  $203.9\ \mu\text{V}/^\circ\text{C}$ , respectively. The output of the ITO/ $\text{In}_2\text{O}_3$  thermocouple reached  $165.7\ \text{mV}$ , and the Seebeck coefficient reached  $138.1\ \mu\text{V}/^\circ\text{C}$  at a  $1200^\circ\text{C}$  temperature difference. Under thermal shock tests, the ITO/ $\text{In}_2\text{O}_3$  thermocouples showed good linearity and repeatability from the test results. The high-temperature annealing atmosphere significantly affected the output curve of the thermocouples, so that the output value reached  $165.9\ \text{mV}$  under a vacuum and  $138.9\ \text{mV}$  in  $\text{N}_2$  conditions, with Seebeck coefficients of  $138.2\ \mu\text{V}/^\circ\text{C}$  and  $115.7\ \mu\text{V}/^\circ\text{C}$ , respectively.

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