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Process Effects on Heat-Sensitive Properties of Sputtered TiO_x Thin Film

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Abstract

Titanium oxide (TiOx) thin films were deposited on K9 glass substrates using a pure titanium target in a dc sputtering system. In this present work, we have investigated the dependence of electrical properties of deposited TiOx thin films on the different process condition, i.e., as the substrate temperature increases from 50 °C to 300 °C, the oxygen partial pressure (pO2) ranged from 2.5% to 10%, the sputtering time increases from 20min to 60min, and annealed in different oxygen concentration atmospheres. The film’s thickness and composition has been performed by profilometer and X-ray Photoelectron Spectroscopy (XPS) respectively. The films’ electrical resistance and the temperature coefficient of resistance (TCR) were studied as a function of the sputtering time, growth temperature, oxygen partial pressure (pO2) and annealing process. The TCR value of the films varied from 0.6% (K-1) to 2.2% (K-1) by controlling deposition process.

Keywords: TiOx thin film, heat-sensitive material, Temperature coefficient of resistance

1. Introduction

Titanium oxide (TiO_x) thin films have attracted considerable attention due to its unique and excellent properties in optics, electronics, sensors and photocatalysis [1-3]. It has a high refractive index and excellent transmittance in the visible and near-infrared range, and a high dielectric constant with physical and chemical stability. Recently study show that titanium oxide (TiO_x) can also be used as a heat-
sensitive material for IR detectors due to its high Temperature coefficient of resistance (TCR) value. Generally, Infrared detectors may be classified into two categories [4]. Thermal IR detectors and photon detectors. Thermal IR detectors have many advantages over photonic detectors: they have a wider spectral response, smaller size and easy to carry because they needn’t cooling system. To achieve high temperature resolution capability, the required characteristics for a suitable uncooled detector material are high temperature coefficient of resistance (TCR), low resistivity, low 1/f noise and silicon processing compatibility. As we know, vanadium oxide (VO_{x}), amorphous silicon Si (a-Si) and semiconducting YBCO (yttrium barium copper oxide) compound are several common heat-sensitive material for conventional IR detectors. Titanium oxide (TiO_{x}) [5] films is a new potential thermal-sensitive material cause its high TCR, chemical stability and physical stability.

Many deposition methods have been reported to prepare Titanium oxide (TiO_{x}) films, such as reactive evaporation method, magnetron sputtering, sol-gel method and pulsed laser deposition [6-9], etc. Reactive magnetron sputtering is one popular method due to its high film deposition rate, high volume and large area uniformity, good repeatability in the fabrication of thin films [10-12]. In this paper, we focus on the relation of TiO_{x} thin films’ electrical properties (sheet resistance, temperature coefficient of resistance) and deposition conditions such as sputtering time, oxygen partial pressure pO_{2}, substrate temperatures and annealing process.

2. Experiment

We obtained the TiO_{x} thin films by the CK-3 magnetron sputtering machine with reactive magnetron sputtering method on K9 glass substrates. Pure titanium (99.99) of 8cm diameter and 4-mm thickness has been used as the sputtering target. High-purity argon (99.99%) and oxygen (99.999%) have been used as the sputtering and reactive gas respectively. The gas flow rates are controlled by D08-2B/ZM gas mass flux controllers (MCF1, MCF2). The vacuum chamber was pumped down to a base pressure of \( 2.0 \times 10^{-3} \) Pa. Argon gas was introduced into the chamber with a flow rate \( \sim 75 \) SCCM. Before the sputtering, we should clean the titanium target surface by pre-sputtering in pure argon atmosphere about 10 min. During the sputtering, the DC power and the working pressure were kept at 100 W and 10 Pa respectively. The substrate temperature and oxygen partial pressure were ranged from 50°C to 300°C and 2.5% to 10% respectively. The sputtered films were then annealed in the chamber in different oxygen concentration atmosphere at 300°C for 30 minutes.

Composition of deposited films has been performed by X-ray photoelectron spectroscopy. The thermal resistances were measured by four-probe resistivity measurement. The relation of resistance versus temperature can be obtained by four-probe resistivity measurement, thermoelectric plate heater and thermocouple detector. We can follow this relation calculate TCR value of TiO_{x} thin film.

3. Results and Discussion

The influence of oxygen partial pressure on composition of TiO_{x} thin films were analyzed by XPS method. Two samples were measured, one of the films was grown at oxygen partial pressure 5% and another at 7.5% pO_{2}. Fig. 1(a) shows the XPS Ti 2p sub-spectra with 5% pO_{2}. Ti 2p3/2 peak and Ti 2p1/2 peak can be found in fig 1(a), located at binding energy 458.5 ev and 464.5 ev, respectively. Fig. 1(b) shows the O 1s spectrum. It is decomposed into peaks centered at 530.1 and 531.3 ev. Fig. 1(c)(d) show the XPS Ti 2p and O 1s spectrum deposited with the 7.5% pO_{2}, respectively. There are Ti 2p3/2 peak and Ti 2p1/2 peak, and binding energy are 459.1 ev and 464.7 ev in fig. 1(c). The O 1s spectrum was decomposed into peaks centered at 530.6, 532.1 and 533.3 ev as shown in Fig. 1(d).
The O/Ti ratio was calculated from the peak area of O 1s and Ti 2p combined with their sensitivity factors. The element ratio of first film is Ti%=38.2%, O%=61.8% and the second film’s is Ti%=34.4 and O%=65.6%. The higher O₂ partial pressure deposited condition, the larger resistance of the film can be obtained. Because the higher concentration of oxygen could cause a more oxidized. According these results, it can be seen that an increase in the pO₂ resulted in a increased in the resistivity and ratio of oxygen element.

Fig. 2 shows the Ln R□ versus T (T is temperature) plots of the TiOₓ samples deposited at 50 °C and different oxygen partial pressures (2.5%, 5%, 7.5%, 10%). The slope of the Ln R□ versus temperature curve gives the TCR value, which is indicated next to each curve on the graph. The TCR and resistance of TiOₓ films increased with the increase in the pO₂ partial pressure during deposition. Films’ sheet resistance increases while the oxygen partial pressure increases, the slope of four diagonal also increases which means the TCR increase. That’s say the resistance of TiOₓ prepared by high oxygen partial pressures changed more obvious and sensitively than low oxygen partial pressures’. This could due to the fact that more oxygen atoms incorporation into the films with the increase in oxygen during deposition. Consequently, an increase oxidation state could be expected compensating the oxygen deficiency in the TiOₓ films.

Figure 3 shows the corresponding TCR values of the TiOₓ films that obtained from the slopes of natural logarithm resistance versus temperature responses. As shown in the figure 3, the TCR values of the films increased from 1.83% (K⁻¹) to 2.2%(K⁻¹)by increasing the substrate temperature during deposition and the pO₂ is 10%. The grain of TiOₓ film increase resulted by the increased of substrate
temperature during deposition. So the grain boundaries density decreases and the grain boundary scattering decreases that carrier concentration and electron mobility increase. That’s why the TCR increase with the substrate temperature during deposition.

![Graph showing variation of TCR with substrate temperatures in TiO_x thin films deposited at various pO_2.](image)

Fig. 3. Variation of % TCR with substrate temperatures in the TiO_x thin films deposited at various pO_2.

Thickneses of deposited films were measure by profilometer. Figure 4 (a) shows the thickness of TiO_x thin films deposited on different sputtering time (20min, 30min, 40min, 50min, 60min). The thicknesses are 94nm, 132nm, 178nm, 231nm, 283 nm with the sputtering time 20min, 30min, 40min, 50min, 60min respectively. Deposition rate is about 4.5nm/min. Further confirmation of thickness in the TiO_x film was carried by SEM, as shown in Fig. 5. The thickness of first sample is about 100nm from Fig 5, and consistent with the result by profilometer. As the figure 4 (b) shows TCR values versus the thickness of the films. It shows that the films thickness also has great influence on the TCR of the TiO_x films. This may due to the film’s structure changed with the thickness. So we should choose the appropriate thickness, to ensure we can get a high TCR value heat-sensitive material.

![Graph showing thickness of deposited TiO_x thin film vs. sputtering time and TCR of deposited TiO_x thin film vs. thickness](image)

Fig. 4. (a)Thickness of deposited TiO_x thin film vs. sputtering time (b) TCR of deposited TiO_x thin film vs. thickness

![SEM image of the TiO_x thin film deposited for 20 minutes](image)

Fig. 5. SEM image of the TiO_x thin film deposited for 20 minutes

It is well-known that the electric properties of intrinsic semiconductors can be changed significantly by annealing process. We have investigated deposition annealing of dc sputtered films in different atmospheres. Figure 6(a) shows the Ln R_0 versus T of the TiO_x films annealed in vacuum atmosphere at 300 °C for 30minutes. Before annealed, the sheet resistance (R_0) is about 500 KΩ at room temperature. After annealed in the vacuum chamber at 300°C for 30minutes, the R_0 decreased to 40 KΩ at room.
temperature. TCR value changed from -1.9% to -0.7% after annealing. This may be due to atoms in the film being able to move freely at 300°C high temperature, and the defect of the film can be eliminated. The electron mobility increase resulted the resistance decreased.

![Image of graph showing temperature vs. TCR and resistance changes](image)

Significant changes in the electrical resistance of the films occur as a result of annealing under oxygen. Polts of Ln R, as a function of oxygen flow rate for the samples unannealed and annealed at 10, 12.5 and 15 SCCM are shown in Fig 6(b). The larger resistance for the film annealed in higher O2 flow rate atmospheres since the higher concentration of oxygen annealed should cause a more oxidized and compensating more oxygen deficiency. The TCR of unannealed film is -1.71%. TCR value was improved and changed into -2.07% after annealed in 10 SCCM oxygen flow rate. However, annealing in 12.5 and 15 SCCM cause the TCR changed into 1.82% and -0.54% respectively. So annealing process can obvious improving the films’ electronic properties.

4. Conclusion

Titanium oxide (TiO2) thin films have been prepared by magnetron sputtering method on K9 glass substrate. According the XPS analysis, an increase in the pO2 resulted in a increased in the resistivity and ratio of oxygen element. Varying preparation conditions was used to modify the TiO2 thin films’ structural and electrical properties to try and optimize the TCR for use as thermal-sensitive material. The increases in the oxygen partial pressure (pO2) and temperature during deposition increased with the TCR from 0.6% (K^-1) to 2.2% (K^-1). The TCR value increases while the pO2 and temperature during the deposition increased. The thickness of TiO2 thin film also has great influence on the TCR. Annealing can also improve the performance as a heat-sensitive material. Therefore, we can optimize the process parameters according to above regularity, to get superior performance TiO2 thin films.
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References


