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The characteristic in infrared region of the TiO₂:Ti film

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Abstract

The TiO_2 :Ti film was prepared as an alternative of the absorber layer for infrared thermal detectors. The asdeposited film was composed of TiO_2 and Ti with a ratio near 5:1. To improve its absorption in infrared region, the film was etched in the diluted H_2O_2 solution. The etching process made the film porous and reduced the concentration of the free electron in the etched film, which decrease the reflection of the films and subsequently increase their absorption. The maximum absorption of the acid-treated Ti-based film was about 90% for the infrared radiation near 1500 cm⁻¹. The resistivity of the etched films has been derived from four probe method with a two-layer model and from infrared spectrum by simulating it with Drude model. The values of resistivity from the two methods are in good agreement. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Uncooled thermal imaging system made of thin film materials have numerous applications in military and civilian filed [1–3]. The infrared detectors made of ferroelectric thin film are heated by radiation and release electric-charges because of the pyroelectricity of the material. Usually, a black layer is grown on the top electrode of a ferroelectric detector to maximize absorption of radiation within the spectral bands of interest.

In bulk ceramic ferroelectric infrared detector, gold-black material is used as black layer [4,5]. For monolithic infrared detector using ferroelectric films, the large heat capacity of gold-black material will increase enormously the time constant of detectors, and subsequently decrease the response speed of detectors. Additionally, it is difficult to pattern the gold-black material into separated sensitive units in craft.

In this article, an infrared absorber layer composed of titanium and titania was prepared using a sputtering combined with a wet chemical solution method. X-ray photoelectron spectroscopy was used to quantify the composition of the film. The scanning electron microscopy (SEM) was used to study the microstructures of the films. The infrared

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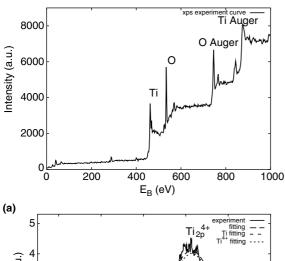
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absorption characteristics of the films were investigated in the reflection spectroscopy and transmission spectroscopy.

2. Structure of the film

The Ti-based films were deposited on SiO_2/Si substrate from a pure titanium target by DC sputtering in argon atmosphere. The film with a thickness of 1.2 μ m was prepared at a deposition rate of 15 nm/min.

X-ray photoelectron spectroscopy for the asdeposited film is shown in Fig. 1. Ti and O peaks are clearly seen in Fig. 1(a). To analyse the valence states of Ti in Fig. 1(b), a double-Lorentz-peak lineshape function like f(E) is used to fit the experiment curve of XPS.



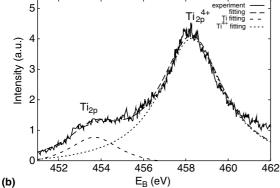


Fig. 1. The XPS curves of as-deposited film: (a) Wide XPS spectra on the surface of the as-deposited films. (b) $\text{Ti}_{2\text{p}_{3/2}}$ XPS spectra and its fitting curves of the as-deposited films.

$$f(E) = y_0 + \frac{2A_1}{\pi} \frac{w_1}{4(E - E_1)^2 + w_1^2} + \frac{2A_2}{\pi} \frac{w_2}{4(E - E_2)^2 + w_2^2}$$
(1)

where y_0 is the offset of the function in y direction, A_1 , A_2 are the areas under the Lorentz peaks respectively, E_1 , E_2 are the positions of the peaks respectively, and w_1 , w_2 the FWHM of the lineshape. The best fitting parameters are: $y_0 = -0.2$; $E_1 = 453.684$ eV; $E_2 = 458.283$ eV; $A_1 = 4.68046$; $A_2 = 23.9995$; $w_1 = 3.07375$ eV; $w_2 = 3.63062$ eV. The two peak positions, E_1 and E_2 , corresponding to the binding energy of $\text{Ti}_{2p_{3/2}}$ and $\text{Ti}_{2p_{3/2}}^{4+}$, are very close to the value of 454.0 and 458.75 eV [6], respectively. The ratio of A_1 to A_2 suggests the composition ratio of Ti and TiO₂ is about 1:5.

In order to increase infrared absorption efficiency of the film, the as-deposited samples were treated in 9% H₂O₂ solution at a temperature of 50 °C. Five samples, which were cut from one TiO₂:Ti/ SiO₂/Si wafer prepared by DC sputtering, were etched for different times 0 (as-deposited film), 270, 330, 390, 510 s respectively. The microstructure of the resultant films were investigated by SEM cross section image (Fig. 2). There is a clear front edge in the film during the etch process. This can be seen in Fig. 2(a) for the film etched for 270 s. Above the edge, the film shows a porous structure. With the increase of etch time, the front edge moved inward while the total thickness of films changes little. In the 510 s etched film, the front edge had reached the surface of the substrate (Fig. 2(b)). The film is more porous than the etched part of the 270 s etched film. It is interesting that the porous structure in the etched films is in nanometer scale.

To find out the origin of oxygen in the films, the experiment process is inspected carefully. The magnetron sputtering system is also used to deposit the oxide films, such as lead lanthanum zirconate titanate. This may be responsible for the existence of TiO₂ in the as-deposited films.

3. Optical and electrical properties of the films

The reflectance in the infrared region of these five samples were shown in Fig. 3. The reflection of

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