

Microstructural characterization of sol-gel derived Ga₂O₃-TiO₂ thin films for gas sensing

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Abstract- Binary TiO₂-Ga₂O₃ thin films were prepared from the sol-gel process. Titanium butoxide and gallium isopropoxide were used as precursor materials. The mixed solution was spun onto the sapphire and silicon substrates at 2500 rpm for 30 s to prepare thin films. The X-Ray Diffraction (XRD) results revealed that the films annealed at a temperature of 500°C for 1 hr is γ -Ga₂O₃ structure. Scanning Electronic Microscope (SEM) images revealed that the film surface is smooth with grains in a nanometer scale. The film showed good responses to 100 ppm, 1000 ppm and 1% O₂ at an operating temperature of 470°C. The resistance of Ga-doped TiO₂ film is between the resistances of pure TiO₂ and Ga₂O₃ films. The response of Ga-doped TiO₂ thin film is sensitive, fast and stable to oxygen gas.

A. Introduction

In the last decade, semiconducting Ga₂O₃ thin films have been investigated for successful realization of a new generation of gas sensors [1] [2]. This sensor operates at comparable high temperatures (800°C-1000°C) and shows high reproducibility, long-term stability and low cross sensitivity to humidity. The sensitivity and selectivity of the pure Ga₂O₃ sensors can be improved by adding certain metals or metal oxides to its surface. The following surface modifications and their effects on the conductivity have been reported, such as Au, SnO₂, Fe₂O₃, Rh₂O₃, RuO₂ and Ir₂O₃ etc. [3]. Pure Ga₂O₃ thin film is a very promising O₂ gas sensor at an operating temperature of 1000°C, while surface modified Ga₂O₃ thin films are sensitive to CO gas and ethanol.

By mixing MoO₃ and TiO₂ compounds it is possible to control the resistance and microstructure of the thin films, ultimately improving the gas-sensing properties [4]. The ionic size (Pauling radius) of Cr⁺³ (0.69 Å), a trivalent dopant is very close to one of Ti⁺⁴ (0.68 Å), therefore, Cr ions can go into the lattice as substitutional metal dopant. The incorporation of Cr in TiO₂ lattice does not affect the crystallography of pure TiO₂ material. Rf-sputtered TiO₂ the films crystalline in the rutile structure during high-temperature annealing in the oxidizing atmosphere at 1170K. No secondary phases resulting from Cr and Nb doping up to 4 at.% Cr and 6 at.% Nb were observed in XRD pattern [5]. The radius of Ga⁺³ is 0.62 Å. It is close to Ti⁺⁴ which could be incorporated into TiO₂ lattice forming acceptor dopant.

The goal of this paper is to study gallium doped TiO₂ thin film, adjust the resistance of Ga₂O₃ thin films in an appropriate range and lower the operating temperature comparing to the pure Ga₂O₃.

B. Experimental

B.1. Sample Preparation:

The precursor solution for sol-gel process was prepared from gallium iso-propoxide (Chemat Technology, Inc. [6]) and titanium butoxide (Aldrich-Sigma) and dissolved in an anhydrous butanol. The spin-coating technique was employed (at a speed of 2500 rpm for 30 sec) to deposit the films onto sapphire substrates with fabricated Pt-film interdigital electrodes on front-side and a Pt-film heater on the backside. As-deposited films were left open in air for 12 hours and subsequently annealed at various temperatures, viz. 400°C, 500°C, 600°C and 700°C, for 1 hr.

B.2. Characterization

The microstructure and the surface topography of the Ga doped TiO₂ films were examined using a XL-30 Scanning Electron Microscope (SEM) operating at 30 kV. The Crystal phase was examined by a wide-angle XRD (Rikagu-D/max-rC) operating at 40 kV and 60 mA. Cu-Kα₁ radiation ($\lambda = 0.154$ nm) and 0.02° angle step were used for the XRD analysis.

B.3. Gas Sensing Characterization

The electrical sensing properties of the Ga₂O₃-TiO₂ thin films to O₂ gas were measured by a computerized multi-meter system (34401A, Hewlett-Packard, USA). The measurements were carried out at different operating temperatures in the range of 150-400°C by applying electrical power to the heater. For O₂ gas sensing, the sensors were exposed to different O₂ gas concentrations (10 ppm to 1%) balanced by dry nitrogen gas. The gas response S is defined as $S = R_{O_2}/R_{O_2(10\text{ ppm})}$, where R_{O_2} is the electrical resistance in different O₂ gas concentrations and $R_{O_2(10\text{ ppm})}$ is the electrical resistance in 10 ppm O₂ gas.

C. Results and discussion

C.1. Characterization

Fig. 1 shows the SEM micrographs of the Ga₂O₃ thin film annealed at 500°C, and Fig.2 shows the SEM micrographs of the Ga₂O₃-TiO₂ thin film annealed at 450°C and 500°C for 1 hr. The figures clearly show that the films are smooth and compact. Fig. 2(a) shows that a crack has occurred at the edge of the film. This is because the thickness of the film at the edge is slightly thicker than in the middle, therefore, it is easy to crack. The grain size is estimated in a range of several nanometers. The thickness of the film is estimated to be 100 nm.

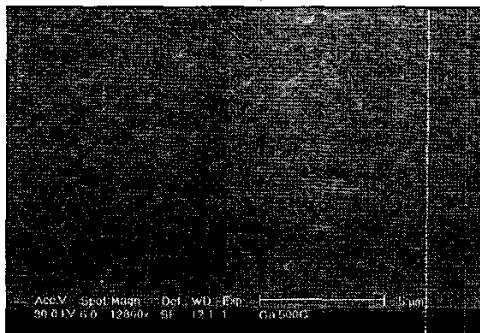


Fig. 1: SEM micrographs of Ga₂O₃ thin films annealed at 500°C, on a Si substrate.

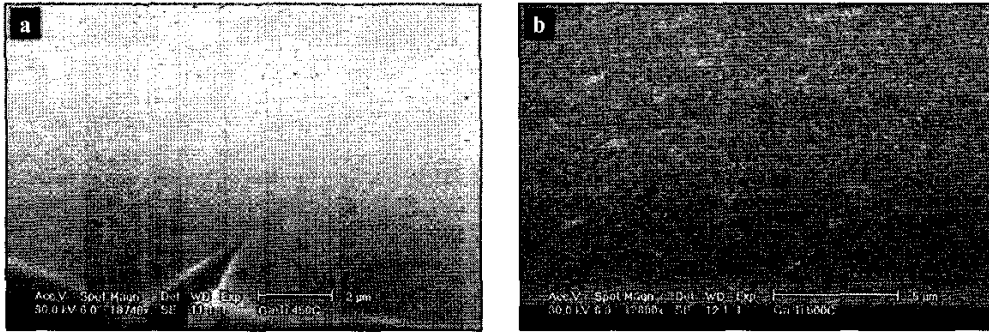


Fig. 2: SEM micrographs of Ga-doped TiO₂ thin films annealed at 450°C(a) and 500°C(b) on Si substrates.

Gallium oxide has several different crystal structures namely α -, β -, δ -, ϵ - and γ -Ga₂O₃. With incorporation of TiO₂ gallium and titanium oxides can form solid solutions such as Ga₂Ti₂O₇ and Ga₂TiO₅. Fig. 3 shows the XRD pattern ($\alpha_0=2^\circ$) of 80% Ga-doped TiO₂ film. The crystal structure is very close to γ -Ga₂O₃ (JCPDS no. 20-426) with a preferential orientation of (004) plane.

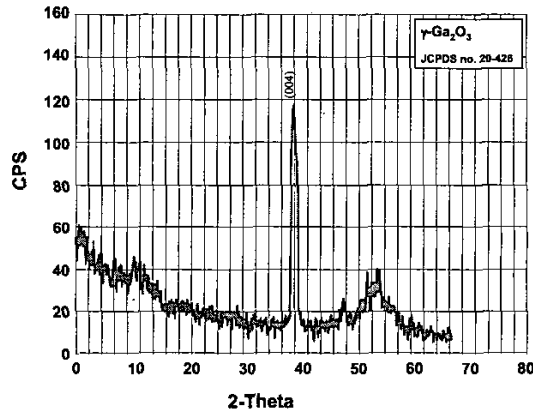


Fig. 3: XRD pattern of the film of 80% Ga-doped TiO₂.

The electrical conductivity of pure Ga₂O₃ films depends on the oxygen partial pressure, irrespective of the film thickness, via a law of the form $\sigma = P_{O_2}^{-1/4}$. It is typical for oxygen-deficient metal oxides, in which single ionized oxygen vacancies dominate [7]. Fig. 4 shows the responses of TiO₂, Ga₂O₃ and gallium doped TiO₂ thin films to 100 ppm, 1000 ppm and 1% oxygen at an operating temperature of 470°C. The baseline is at an oxygen concentration of 10 ppm in nitrogen. The resistance of Ga-doped TiO₂ film is between the resistances of pure TiO₂ and Ga₂O₃ films. The response of Ga-doped TiO₂ thin film is sensitive, fast and stable to oxygen gas.

The oxygen response shows that the acceptor behavior of Ga (doped TiO₂) causes a change from n-type to p-type conductivity when 80% Ga is incorporated in the TiO₂ thin films. Assuming that Ga is incorporated substitutionally the incorporation mechanism using Kröger's notation can then be described as follows:

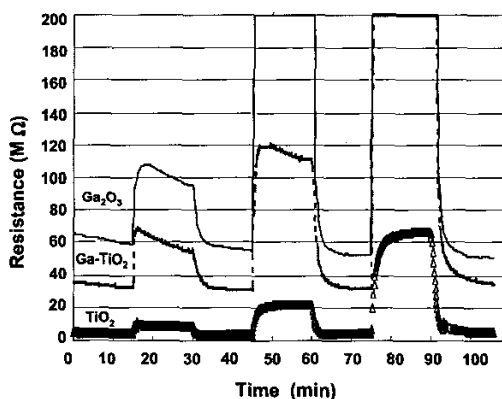
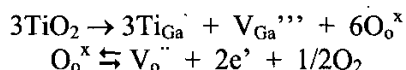


Fig. 4: The responses of pure TiO_2 , 10% Ga-doped TiO_2 and pure Ga_2O_3 thin films to 100 ppm, 1000 ppm and 1% oxygen gas concentrations at an operating temperature of 470°C .

D. Conclusions

Binary TiO_2 - Ga_2O_3 thin films have been successfully prepared by the sol-gel process. The XRD results revealed that the films annealed at a temperature of 500°C for 1 hr is γ - Ga_2O_3 structure. SEM images showed that the film surface is smooth with grains in a nanometer scale. The resistance of Ga-doped TiO_2 film is between the resistances of pure TiO_2 and Ga_2O_3 films. The response of Ga-doped TiO_2 thin film is sensitive, fast and stable to 100 ppm, 1000 ppm and 1% O_2 at an operating temperature of 470°C . Further studies of the binary Ga_2O_3 - TiO_2 system to other oxidizing and reducing gases are being undertaken in our Lab.

Acknowledgments

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