研究報告

Electrical and Humidity Sensitive characteristics of TiO_2 and $\text{TiO}_2\text{—SnO}_2$ Films Prepared by Sol—Gel Method

by

Noboru YOSHIMURA* Shigeki SATO** Masashi ITOI* and Haruo TAGUCHI**

ABSTRACT

TiO_2 and $\text{TiO}_2\text{—SnO}_2$ thin films were prepared by sol-gel method using the metal alkoxides ($\text{Ti}(\text{O}-i\text{-Pr})_4$, $\text{Sn}(\text{OEt})_4$). These films have been successfully prepared in low temperature of about 500°C . The electrical properties are semiconductive. A humidity sensor with TiO_2 and $\text{TiO}_2\text{—SnO}_2$ films was prepared to use at high relative humidity above 60% RH. It is found that a response property of the sensors for the time is very fast between 30% RH and 90% RH as compared with that for other sensors.

Key Words : Sol-gel method, TiO_2 and $\text{TiO}_2\text{—SnO}_2$ thin films, Humidity sensor, Electrical property

INTRODUCTION

According as increasing of demand for home electronics manufactures, humidity and dew condensation sensors have been required for precision parts such as VTR head, optoelectronics device and so on.

In this study, the TiO_2 and $\text{TiO}_2\text{—SnO}_2$ were selected because of high sensitivity for the humidity and superior response property for the time. We tried to prepare a ceramic thin film sensor using sol-gel method. Ceramic thin films are generally prepared by CVD and PVD, but those methods involve several problems such as the uniformity of the films and the preparation cost. Recently, the sol-gel method has been of great interest as a technique to prepare new thin films. The sol-gel method can obtain colloidal solvent or precursor compound when the metal alkoxides are hydrolyzed under the controlled conditions ; pH, additional H_2O , solvent and catalyst. The thin film coating on a substrate is achieved by dipping and withdrawing method. The prepared thin films are estimated by synthetic analysis (XRD, TG-DTA, IR).

This paper deals with the electrical and humidity sensitive characteristics of TiO_2 and $\text{TiO}_2\text{—SnO}_2$ films prepared by sol-gel method using the metal alkoxides.

Received August 25, 1990

* Department of Electrical Engineering, Mining College, Akita University, 1 - 1 Tegatagakuencho, Akita

** TDK Co., Ceramics Division, Nikahomachi, Hirasawa, Yuri - Districk, Akita-Prefecture

EXPERIMENTS

Specimen Preparation

The preparation method of TiO_2 sol solution referred the paper : T. Yoko et al¹⁾. The metal alkoxides ($\text{Ti}(\text{O}-i\text{-Pr})_4$ tetra isopropoxi titanata ; TIPT), anhydrous $\text{C}_2\text{H}_5\text{OH}$, distilled water and HCl solution as the catalyst were used as the TiO_2 sol solution. At first, half of the precibed amount for anhydrous $\text{C}_2\text{H}_5\text{OH}$ was slowly added in TIPT, and the solution was mixed for 30 minutes. Secondly, the rest amount of $\text{C}_2\text{H}_5\text{OH}$ was introduced into H_2O and HCl with the concentration of 8.26mol%. The $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}-\text{HCl}$ solution was slowly dropped into TIPT- $\text{C}_2\text{H}_5\text{OH}$ one with a buret in mixing, and TIPT was hydrolyzed slowly at room temperature. After the titration of the hydrolystic solution, the solution was mixed for 30 minutes.

On the other hand, in the case of TiO_2 - SnO_2 sol, at first, $\text{Sn}(\text{O}-\text{Et})_4$ (tetra etoxitinate ; TET) and anhydrous $\text{C}_2\text{H}_5\text{OH}$ were mixed. Where TET has the concentration of 0.1g/ml. The TET- $\text{C}_2\text{H}_5\text{OH}$ was maintained at 70°C for 120 minutes. Because TET didn't dissolve in $\text{C}_2\text{H}_5\text{OH}$ at room temperature. Secondly, the base sol was prepared from TiO_2 one after the HCl solution was added. Finally, the TET- $\text{C}_2\text{H}_5\text{OH}$ solution was added into the base sol. After the addition, the TiO_2 - SnO_2 sol solution was mixed for 30 minutes.

The TiO_2 and TiO_2 - SnO_2 thin films were coated by dipping-withdrawing method on the Al_2O_3 and/or coaing #7059 glass substrate in N_2 gas flowing. The withdrawing speed was kept constant at 10mm/min.. The thickness of the films was about $0.75\mu\text{m}$ for TiO_2 , and about $0.2\mu\text{m}$ (SnO_2 ; 10%), and $0.15\mu\text{m}$ (SnO_2 ; 30%) for TiO_2 - SnO_2 for fifth times application.

Among the preparation and coating process of fifth times, the operation was carried out in N_2 gas. The flow chart of the sol preparation and the film coating is shown in Fig. 1.

Measurement

The thin film structures were observed by a scanning electron microscope (SEM). The contamination of organic and OH substances in the thin films was identified by IR spectroscopy.

The crystalline phases against the heat treatment temperature were identified by X-ray diffraction (XRD) using $\text{Cu}-\text{K}\alpha$ radiation. The transitions of gel on the crystalline form were identified by TG-DTA technique.

For the measurement of electrical conductivity, the gold was evaporated on the thin film's surface as the electrode. The electrical conductivity of the film was measured due to d. c. two-terminal method.

Fig. 1 Flow chart of the sol-gel method

Fig. 2 A shape of sensor

In the case of humidity sensor, the gold electrode was evaporated like a comb on the film's surface, as shown in Fig. 2. The impedance of the sensor was measured by an a. c. circuit shown in Fig. 3. Where a. c. voltage with the frequency of 1kHz was 7.41 V_{rms}. A digital multimeter (Advantest R 6551) was used to measure the a. c. voltage. A chamber under the controlled temperature and humidity (Tabai PSL-2) was used to measure the impedance for TiO_2 and $\text{TiO}_2\text{-SnO}_2$ sensors.

RESULTS AND DISCUSSION

Thin Film Structure

The TiO_2 and $\text{TiO}_2\text{-SnO}_2$ thin film structures were observed with SEM. The SEM photographs of TiO_2 and $\text{TiO}_2\text{-SnO}_2$ thin films are shown in Fig. 4. The SEM photographs indicate that the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ thin films prepared by sol-gel method have very uniformity structure.

Fig. 4 (a) SEM photograph of TiO_2 film ($\gamma = 7,500^\circ\text{C}$ anneal) prepared by sol-gel method

Fig. 4 (b) SEM photograph of $\text{TiO}_2\text{-SnO}_2$ (30%) thin film annealed at 500°C

Fig. 3 Measurement circuit and system for TiO sensor

Thin Film Contamination

The IR spectra of the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ thin films are shown in Fig. 5. From Fig. 5, it is found that the thin films at the low heat treatment temperature contain the organic and OH substances. The Ti-O and Sn-O adsorption peaks increase with the heat treatment temperature. For the reason, the heat treatment temperature is required above 500°C .

Crystalline Phase

The TiO_2 and $\text{TiO}_2\text{-SnO}_2$ up to 30mol% were found to be anatase and/or rutile crystalline phase form

300°C to 500°C, as shown in Fig. 6. In $\text{TiO}_2\text{-SnO}_2$ (30mol%), SnO_2 was not solid solution in TiO_2

Fig. 5 (a) Changes in IR spectra TiO_2 gel film with heat treatment temperature

Fig. 5 (b) Changes in IR spectra $\text{TiO}_2\text{-SnO}_2$ gel film with heat treatment temperature

Fig. 6 (a) Changes in X-ray diffraction patterns of TiO_2 gel powder with heat treatment temperature Fig. 6 (b) Changes in X-ray diffraction patterns of $\text{TiO}_2\text{-SnO}_2$ gel powder with heat treatment temperature

A typical TG-DTA curve for the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ gel powders is shown in Fig. 7. It is found from the analysis for the TiO_2 gel that a broad endothermic peak between 100°C and 200°C is due to dehydration. A low pitched exothermic is due to the combustion of the organic substance contained in the gel. On the other hand, for the $\text{TiO}_2\text{-SnO}_2$ film, it is considered that the sharp exothermic peak at 435°C is due to the combustion of the alcohol or organic substance (carbon, alkyl groups). The properties strongly depend on the gel preparation process.

Electrical Conduction

Fig. 7 (a) DTA and TG curve of TiO_2 gel powder

Fig. 7 (b) DTA and TG curve of $\text{TiO}_2\text{-SnO}_2$ gel powder

Figures 8 (a) and (b) show the temperature dependence of electrical conductivity on the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ films after the heat treatment. It is clearly seen that the films depend on the heat treatment temperature and give semiconductive characteristics. The electrical conductivity of the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ films decrease with the heat treatment temperature. At below 500°C , this reason is to remove the impurity in

the gel. On the other hand, at above 500°C , the properties may be determined due to the difference of the density of the lattice defect. Because the electrical conduction for the TiO_2 film causes by the nonstoichiometric composition. Moreover, it seems from Figs. 8 (a) and 8 (b) that the increase of electrical conductivity of the film is determined by SnO_2 doped in TiO_2 .

Fig. 8 (a) Temperature dependence of film conductivity on TiO_2 with heat treatment at γ -7

Fig. 8 (b) Temperature dependence of film conductivity on $\text{TiO}_2\text{-SnO}_2$ (30%) with heat treatment at γ -7

Humidity - sensitive Characteristics

In general, the electrical conductivity of the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ films changes with physisorbed and/or chemisorbed water on the semiconductive ceramics surface under the humid atmosphere condition. The impedance of the TiO_2 and $\text{TiO}_2\text{-SnO}_2$ films against the humidity is shown in Fig. 9. The property for TiO_2 and $\text{TiO}_2\text{-SnO}_2$ was nonlinear from 30%RH to 90%RH. As the relative humidity increased from about 60%RH to 90%RH, the impedance fell down rapidly. It seems that the effect of spread of sensitivity is owing to SnO_2 doped in TiO_2 . From a typical data in Fig. 9, the decrease of 86.1% was found when the relative humidity changed from 30%RH to 90%RH at 20°C . The humidity dependence of the capacitance

Fig. 9 Changes in impedance on TiO₂-SnO₂ sensor with relative humidity at 20°C

and the dissipation factor ($\tan \delta$) of the films were measured in order to understand its sensitive mechanism. Fig. 10 shows the change in the capacitance and the dissipation factor with the relative humidity. The capacitance and the dissipation factor increased above 60% RH. This increasing point is equivalent to one at where the impedance and the dissipation factor increase. It is considered that the impedance of the sensor decreases with increasing the electrical conductivity and the capacitance of the films due to polar molecules (H₂O) adsorbed on the surface of the sensor.

Fig. 11 shows the response curve of the TiO₂ system sensor. The response of TiO₂ system sensor for the humidity is reasonable. The output voltage of the sensor becomes stationary state within 100 seconds. But the response property becomes late with doping SnO₂. The response for the desorption process is faster than that of the adsorption one. The response property for the time constant is shown in Table. 1. The time constant is one which becomes 63.2% of the stationary state. The results show that a response property of the sensors for the time is very fast between 30%RH and 90%RH, as compared with that for other sensors. It is presumed that those properties are account of nonlinear sensitivity for the humidity.

Fig. 10 Changes in capacitance and $\tan \delta$ with relative humidity on TiO₂-SnO₂ sensor

Fig. 11 Response property of sensor on $\text{TiO}_2\text{-SnO}_2$ system

Table. 1 Time constant of humidity sensor

kind of sensor	Time constant [sec] desorption/absorption	test range of RH
TiO_2	2.2/2.2	30%~90%
$\text{TiO}_2\text{-SnO}_2$ (10%)	6.3/2.2	30%~90%
$\text{TiO}_2\text{-SnO}_2$ (30%)	5.0/3.3	30%~90%
ZrO_2 system	18/31	33%~53%/84%~53% Ref. 2)
SiO_2 system	8.9/3.3	50%~90% Ref. 3)
polymer system	below 1sec	30%~90% Ref. 4)

CONCLUSION

The TiO_2 and $\text{TiO}_2\text{-SnO}_2$ thin films were prepared by sol-gel method using metal alkoxides in low temperature. The electrical properties are semiconductive.

The sensitivity for the humidity on the TiO_2 system sensor shows that the impedance decreases in high humidity. The humidity response of the sensor is very fast and excellent. The $\text{TiO}_2\text{-SnO}_2$ sensor is easily produced by sol-gel method, and expected as dew condensation sensor with high sensitivity.

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