Humidity-Sensitive Properties of Titania Films Prepared Using the Sol-Gel Process

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ゾル-ゲル法で作製した酸化チタン薄膜の感湿特性

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TiO₂ films, as well as powders as reference, were prepared using the sol-gel process, using titanium isopropylalkoxide (TIPT) as a precursor. The films were deposited on glass slides and heated either to 300°C or to 500°C. The morphology of the film surface was observed using scanning electron microscopy (SEM). Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS) at different relative humidities were carried out to study the possibility of using sol-gel processed titania films as detecting elements in humidity sensors. A good resistance versus relative humidity (rh) sensitivity was observed in the range from 50% to 85% rh. The response time of titania films was rather fast, estimated in a few seconds.

Key-words : Humidity sensors, Titania, Sol-gel, Film, Electrical properties

1. Introduction

Miniaturization of sensors is required for on-chip integration technology, which is becoming increasingly important in sensor production.¹⁾ Fabrication technologies of microelectrodes, such as sputtering, chemical etching, thick- and thin-film preparations, have been used to develop various chemical sensors.²⁾ Ceramic materials are suitable for application to chemical sensors.³⁾

Recent progress in ceramic deposition technologies, mainly driven by the continuous advancement of microelectronics, provides new possibilities for development of ceramic active elements in the field of chemical sensors. The sol-gel method is very attractive for the preparation of very uniform ceramic powders, with high purity and a very homogeneous distribution of the components on the atomic scale. But

probably its most promising feature is the possibility of powder-free processing of ceramics in their final shape, like fiber or film,⁴⁾ which can be used as active elements in sensing devices. Another advantage which may be derived from the use of sol-gel processing in sensor manufacturing technology, is a deposition method less costly than the others currently used to produce ceramic films. Recently, studies on the application of the sol-gel technique to the production of optical⁵⁾⁻⁷⁾ and chemical^{8),9)} sensing devices have been reported in the relevant literatures.

In the field of humidity sensors, more studies have been made of polymer films than of ceramic films.¹⁰⁾ Only a few ceramic oxides have been investigated in thin-film form,¹¹⁾⁻¹³⁾ or in films prepared by sol-gel method.^{14),15)} Several attempts have been made to develop microchip humidity sensors using integrated circuit technology, based on ceramic sensing elements.¹⁶⁾⁻²⁰⁾

The use of either sintered porous compacts or thick films of titania and doped-titania as sensing elements for humidity-measurement devices has shown promise in the literature.²¹⁾⁻²⁷⁾ This paper deals with the processing of TiO₂ films using the sol-gel technique. Chemical, microstructural and electrical analyses were carried out in order to study the possibility of using titania films as detecting elements in a sensor device suitable for hybrid electronic integration.

2. Experimental procedure

2.1 Materials

Titanium isopropylalkoxide (TIPT) was used as the precursor compound for the sol-gel process. The starting solution was prepared by mixing TIPT (Aldrich), isopropanol (Aldrich), distilled water and HCl (37%) as a catalyst, with molar ratios of 1: 21:

1: 0.11. The solution was stirred for 10 min.

From this solution, bulk gels and films were obtained. The bulk was dried in an oven for one day at 100°C, powdered, heated to different temperatures and then analyzed. The films were deposited on commercial glass microscope slides, previously carefully cleaned. The slides were dipped into the solution and withdrawn at a speed of 0.07 cm/min. The films were dried in an oven at 100°C for 30 min. Afterwards, the samples were heated either to 300°C or to 500°C, at a heating rate of 100°C/h in an oven, and then were immediately allowed to cool to room temperature in the same oven. In order to study their electrical properties, gold electrodes 200 nm thick, 100 μm wide and spaced 40 μm apart, were deposited on the sensitive film by evaporation, and defined by a standard photolithographic process.

2.2 Measurements

In order to study the preparation procedure, the powders obtained from the bulk gels were studied by Fourier transform infrared (FTIR) spectroscopy (Nicolet model 5PC), X-ray diffraction analysis (XRD), performed with a Philips model PW 1050, using Cu K α radiation ($\lambda=0.154$ nm), and X-ray photoelectron spectroscopy (XPS), using an Escalab Vacuum Generator (VG).

All X-ray photoelectron spectra were recorded in the fixed analyzer transmission (FAT) mode with a pass energy of 20 eV, using Al K $\alpha_{1,2}$ radiation as an excitation source ($h\nu=1486.6$ eV). All measurements were performed at a residual pressure of 10^{-9} Pa. The binding energy (b.e.) scale was calibrated using the 4f $_{7/2}$ gold signal at 83.7 eV. Corrections of the energy shift due to the steady-state charging effect of the samples were carried out by referencing to the C 1s line (b.e.=285.0 eV) from the residual pump-line oil contamination. The accuracy of the b.e. values measured was ± 0.2 eV, and the reproducibility of the results was within these values. The spectra were collected by a DEC PDP 11/83 data system and data handling software provided by the spectrometer manufacturer (VG 5000 processing software).

The films were analyzed by XPS, by scanning electron microscopy (SEM; Jeol model 6300), and by electrochemical impedance spectroscopy (EIS), using a Solartron model 1255 frequency response analyzer equipped with a high impedance adaptor built by us. Impedance spectra were recorded in the frequency range from 10^{-2} to 10^5 Hz, at 40°C, at relative humidity (rh) values ranging from 5% to 85%. The resistance values were calculated on the complex plane plot from the intercepts of the semiarc at high frequencies, extrapolated where necessary, with the real axis.¹²⁾

Stability tests and response time measurements were also performed. EIS measurements over the entire rh range tested were repeated at different time intervals after keeping the specimens 12 h at 5% rh.

Response time tests were performed by measuring the current for 0.5 V dc potential application, during rh cycling, using a Keithley Quasistatic CV-meter 595.

3. Results and discussion

Figure 1 shows the typical morphology of the titania films heated to 500°C. SEM observations showed that films were compact, free of porosity, made up of quite uniform particles less than 100 nm in diameter. The films heated to 300°C showed practically the same morphology. SEM observations confirmed that the films were about 0.3–0.4 μm thick, as measured using a surface roughness meter. These thicknesses are in line with those reported in the literature for similarly prepared titania coatings.²⁸⁾

Figure 2 shows the FTIR spectra of the powdered bulk gel, heated to different temperatures up to 500°C. The large peak at 1000–400 cm^{-1} is attributa-

Fig. 1. SEM micrograph of the surface of the TiO $_2$ film heated to 500°C.

Fig. 2. IR spectra of TiO $_2$ powders heated to different temperatures.

ble to the Ti–O bond, according to the results reported in the literature.²⁹⁾ All the other peaks are attributable to the organic compounds remaining in the gel. These peaks decrease in intensity with increasing temperatures, and they disappear when the temperature reaches 500°C. The higher the temperature, the sharper the peak attributed to the Ti–O bond.

Figure 3 shows the XRD patterns of the powdered bulk gel, heated to different temperatures up to 500°C. Below 200°C, the diffraction patterns showed a lack of any definite structure. The anatase structure appears above 250°C. Similar results have been reported by other authors for a gel with composition between 90% and 100% of TiO₂ prepared with a similar method.³⁰⁾ The crystallinity of the specimens increases with increasing temperatures, up to 500°C when the powder is fully crystalline. Raman spectroscopy investigations, carried out by some of the authors of this paper and reported elsewhere,³¹⁾ confirmed that the anatase phase is present and well formed already at 350°C, showing a well-defined peak in the region 145–160 cm^{−1}. Standard XRD analysis carried out on TiO₂ films heated up to 500°C did not reveal any definite structure. However, XRD tests performed using very low scanning rate on films deposited on quartz substrate and heated to 900°C, showed broad peaks of an oriented anatase structure. This may suggest a slower crystallization for TiO₂ films than for TiO₂ powdered bulks.

Table 1 shows the Ti 2p and O1s binding energy (b.e.) values (in eV) measured on both powders and films heated to 300°C and 500°C. The analysis of the

Table 1. XPS binding energy (eV) for the specimens analysed, with quantitative percentage of the three components of the O1s line and FWHM of the Ti 2p line.

Specimen	Ti 2p		O 1s		
		(FWHM)	TiO ₂	-OH	H ₂ O
powder 300°C	458.5	1.84	530.0	531.2	532.3
			(78%)	(14%)	(8%)
powder 500°C	458.9	1.65	530.2	531.8	532.6
			(82%)	(9%)	(9%)
film 300°C	458.5	1.64	529.9	531.5	532.9
			(53%)	(25%)	(22%)
film 500°C	458.5	1.51	529.7	531.4	532.6
			(62%)	(22%)	(16%)

Ti 2p spectra of all the specimens shows b.e. values which are characteristic of the element in its Ti⁴⁺ oxidation state.³²⁾ Table 1 also gives the full width at half maximum height (FWHM) values for the Ti 2p peak: one can observe that the width of the line increases with decreasing crystallinity in the specimens. However, the line widths are larger for the powdered specimens than for films. This can be explained in terms of the smoother surface of the films: the surface roughness of powdered specimens can produce different static charging effects which cause a broadening of the line width.³³⁾

In the O1s region, all the specimens exhibited a complex band, for which curve fitting showed the presence of three components centered at b.e. values around 530, 531.5 and 532.6 eV (Fig. 4). The first component is attributable to TiO₂, in addition to a small part due to instrumental oxygen contamination. In fact, the quantitative O/Ti ratios obtained by using this O1s component and the Ti 2p line (between 2.1 and 2.3 for all the specimens) are close to the theoretical value. The components at 531.5 eV and at 532.6 eV are usually attributed to hydroxyl groups and to water molecules, respectively.³⁴⁾ As shown in Table 1, the quantities of the two components at higher b.e. values are larger for samples heated to 300°C and for films than for powders. The presence of a larger amount of water and of more hydroxyl groups in films than in powders may be at-

Fig. 3. XRD patterns of TiO₂ powders heated to different temperatures.

Fig. 4. XPS O1s peaks of the powder heated to 500°C (a), of the film heated to 300°C (b), and of the film heated to 500°C (c).

tributed to the drying times of the specimens, which were 30 min for films and 1 day for powders. Also the crystallinity of the samples has to be considered, given that the less ordered the sample, the larger the number of water molecules and hydroxyl ions. XPS analysis performed on the films left in the test chamber for 1 day showed a decrease in the intensities of the two components of the O1s line at higher b.e. values, confirming the attribution made.

EIS spectra collected on films at rh values lower than about 30% showed one inclined semicircle, which did not start from the origin of the complex plane axes. At higher rh, EIS spectra also showed another inclined semicircle at low frequencies, as shown in Fig. 5, where the complex impedance spectrum of the film heated to 500°C at 85% rh is reported. Therefore, the equivalent circuit model of titania films can be assumed to be made up of three elements in series: one resistive and two RC elements. In accordance with the findings of other authors,²⁴⁾ the resistive element, which is independent of rh, is characteristic of the bulk. It was measured to be about 10 k Ω . The RC element at higher frequencies, which is rh-dependent, is characteristic of the grain surface. Given the generally accepted ionic conduction mechanism for ceramic oxides in humid environments,¹⁰⁾ the observed decrease in resistance with increasing rh is due to the increasing number of water molecules present on the surface. The RC element at low frequencies, which also depends on rh, is attributable to polarization effects at the film-electrode interface. This effect occurs because gold electrodes are blocking for mobile conduction ions, which accumulate at the electrode interface when the number of carriers arriving at or departing from the electrode is too large to be kept up by the electrode reactions.²⁴⁾ We observed that this polarization effect depends on the geometry of the electrodes and the materials used. With the geometry adopted in our tests and the use of sputtered gold electrodes, polarization at the highest rh was much lower than that showed in similar conditions by spinel thin-films

Fig. 5. Complex impedance plot of the TiO₂ film heated to 500°C, at 85% rh.

Fig. 6. Rh-dependence of titania films resistance at 40°C.

with chromium electrodes.¹³⁾

Figure 6 shows the rh-dependence of resistance for titania films heated to 300°C and 500°C. Both specimens showed similar behaviour: a small resistance variation from 0% to about 50% rh, and a good resistance versus rh sensitivity, of two orders of magnitude, in the range from 50% to 85% rh, with a good exponential relationship. The resistance of the specimens heated to 500°C is higher than that of specimens heated to 300°C over the entire rh range.

The rh-dependence of electrical conductivity for ceramic oxides has been widely recognized as related to the water adsorption mechanism on the surface of the oxides.¹⁰⁾ At low rh, conduction is due to proton hopping between hydroxyl ions on the first layer of chemisorbed water, whereas at high rh protons hop between physisorbed water molecules. Protons may arise from dissociation of hydroxyls and of water. The activation energy required to dissociate hydroxyl ions is higher than that needed to dissociate water molecules, thereby resulting in higher resistivity at low rh. At high rh, a higher carrier concentration is found when more than one layer of physisorbed water molecules is present on the oxide surface. These molecules are singly bonded and form a liquid-like network, which greatly increases the dielectric constant.³⁵⁾ The increased dielectric constant promotes dissociation by lowering dissociation energy, which thus causes the increase in proton concentration.³⁶⁾ Thus, the lack of sensitivity at low rh values is related to the microstructural features of the specimens. When the surface area is small, as for dense films, the number of adsorbed water molecules is also very small. This may explain the relationship between rh variations and the logarithm of the resistance observed for sol-gel processed titania films. This explanation has, in fact, already been given for a similar trend observed for dense MgAl₂O₄ thin-films.³⁷⁾ Better sensitivities at low rh were observed for porous pellets of MgAl₂O₄ with a wide pore-size distribution by some of the authors of this

paper.³⁸⁾ Also in the case of porous titania pellets, the results of other authors²²⁾ have shown that the presence of porosity guarantees a better sensitivity at low rh. However, it must be kept in mind that, at low rh, impedance values of the same order of magnitude as the instrumental input impedance ($10^{11} \Omega$) were recorded. The very high resistivity values measured may make them not entirely reliable.

Higher resistance values were measured on the films heated to 500°C. Although both films have shown similar microstructures at SEM observations and are both rather dense, a decrease in the amount of adsorbed water may explain the higher resistivity of the films heated to 500°C. In fact, the higher firing temperature of the films causes the more ordered structure of the films heated to 500°C, accompanied by a decrease in their surface area and by a shift of average pore size towards larger values, and may be responsible for the lower number of hydroxyl ions and water molecules initially present on their surface, as demonstrated by XPS analysis, particularly at low rh. Less water can be adsorbed by these samples, resulting in higher resistivity over the entire rh range.

Fig. 7. Log resistance versus rh curves for the film heated to 300°C, measured at different time intervals.

Fig. 8. Log resistance versus rh curves for the film heated to 500°C, measured at different time intervals.

Fig. 9. Effect of rh cycling on the current response of the film heated to 300°C, solid line for I and dotted line for rh.

Reproducibility tests were performed by maintaining the films for 12 h at 5% rh before each cycle of EIS measurements over the rh range tested. As shown in Figs. 7 and 8, the films heated to 300°C exhibit better reproducibility at rh values higher than 50%, while films heated to 500°C behave better at rh lower than 50%. These results may also be related to XPS findings: the films heated to 300°C have a tendency at low rh to loose some of the water molecules initially present. The films heated to 500°C may tend at high rh to have an increased number of water molecules more strongly bonded to the surface.

These results indicate that a proper activation treatment is necessary to improve the TiO_2 film's electrical behaviour, both in terms of sensitivity and reproducibility over the entire rh range.

Response time measurements showed that TiO_2 films respond promptly to a cyclic variation of rh. The estimated response time is only a few seconds. After an initial drift, good reversibility and stability are observed (Fig. 9).

4. Conclusions

Their electrical characteristics make TiO_2 films prepared using the sol-gel process candidates for use as sensing elements in humidity-measurement devices. Their exponential response at rh higher than about 50% and their short response time support this conclusion. Their high resistivity and their lack of sensitivity at low rh are, however, significant problems which are still to be resolved. These problems can probably be overcome by doping and by a suitable activation process. It seems extremely important to emphasize that doping can easily be carried out using the sol-gel preparation method.

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References

- 1) S. C. Chang and W. H. Ko, "Sensors: A Comprehensive Survey", Ed. by W. Göpel, J. Hesse and J. N. Zemel, VCH, Weinheim (1989) pp. 169-94.
- 2) C. C. Liu, Techn. Dig. of 4th Intern. Meet. on Chemical Sensors, Tokyo, Japan, Sept. 13-17, 1992, Japan Ass. of Chemical Sensors, pp. 2-5.
- 3) J. Arndt, "Sensors: A Comprehensive Survey", Ed. by W. Göpel, J. Hesse and J. N. Zemel, VCH, Weinheim (1989) pp. 248-78.
- 4) J. C. Brinker and G. W. Scherer, "Sol-Gel Science", Academic Press, San Diego (1990) pp. 839-80.
- 5) V. Chernyak, R. Reisfeld, R. Gvishi and D. Venezky, *Sens. Mater.*, **2**, 117-26 (1990).
- 6) A. J. Martin and M. Green, *Proc. SPIE-Int. Soc. Opt. Eng.*, **1328**, 352-63 (1990).
- 7) K. T. V. Grattan, G. E. Badini, A. W. Palmer and A.C.C. Tseung, *Sens. Actuators A*, **A26**, 483-87 (1991).
- 8) G. C. Frye, J. C. Brinker, A. J. Ricco, S. Martin, J. Hilliard and D. H. Doughty, *Mater. Res. Soc. Symp. Proc.*, **180**, 583-93 (1990).
- 9) J. I. Dulebohn, S. C. Haefner, K. A. Berglund and K. R. Dunbar, *Chem. Mater.*, **4**, 506-08 (1992).
- 10) B. M. Kulwicki, *J. Am. Ceram. Soc.*, **74**, 697-708 (1991).
- 11) Y. Nabeta, K. Suzuki and T. Inuzuka, "Chemical Sensors", Ed. by T. Seiyama, K. Fueki, J. Shiokawa and S. Suzuki, Kodansha, Tokyo and Elsevier, Amsterdam (1983) pp. 410-15.
- 12) G. Gusmano, G. Montesperelli, E. Traversa, A. Bearzotti, A. D'Amico and C. Di Natale, *Sens. Actuators B*, **B7**, 460-63 (1992).
- 13) G. Gusmano, G. Montesperelli, E. Traversa and G. Matogno, *J. Am. Ceram. Soc.*, **76**, 743-50 (1993).
- 14) N. Yoshimura, S. Sato, M. Itoi and H. Taguchi, *Sozai Busseigaku Zasshi*, **3**, 47-56 (1990).
- 15) G. Vaivars, J. Pitkevics and A. Lasis, Techn. Dig. of 4th Intern. Meet. on Chemical Sensors, Tokyo, Japan, Sept. 13-17, 1992, Japan Ass. of Chemical Sensors, pp. 128-31.
- 16) M. G. Kovac, D. Chieck and P. Goodman, *Solid State Technol.*, **21**, 35-39 (1978).
- 17) P. P. L. Regtien, *Sens. Actuators*, **2**, 85-95 (1981/82).
- 18) R. S. Jachowicz and S. D. Senturia, *Sens. Actuators*, **2**, 171-86 (1981/82).
- 19) S. L. Garverick and S. D. Senturia, *IEEE Trans. Electron Devices*, **ED-29**, 90-94 (1982).
- 20) M. Parameswaran, H. P. Baltes, M. J. Brett, D. E. Fraser and A. M. Robinson, *Sens. Actuators*, **15**, 325-35 (1988).
- 21) K. Katayama, T. Akiba and H. Yanagida, "Chemical Sensors", Ed. by T. Seiyama, K. Fueki, J. Shiokawa and S. Suzuki, Kodansha, Tokyo and Elsevier, Amsterdam (1983) pp. 433-38.
- 22) Y. C. Yeh, T. Y. Tseng and D. A. Chang, *J. Am. Ceram. Soc.*, **72**, 1472-75 (1989).
- 23) T. Yamamoto and K. Murakami, "Chemical Sensor Technology, Vol. 2", Ed. by T. Seiyama, Kodansha, Tokyo and Elsevier, Amsterdam (1989) pp. 133-49.
- 24) Y. C. Yeh, T. Y. Tseng and D. A. Chang, *J. Am. Ceram. Soc.*, **73**, 1992-98 (1990).
- 25) K. Katayama, K. Hasegawa, T. Takahashi, T. Akiba and H. Yanagida, *Sens. Actuators A*, **A24**, 55-60 (1990).
- 26) K. Katayama, K. Hasegawa, T. Noda, T. Akiba and H. Yanagida, *Sens. Actuators B*, **B2**, 143-49 (1990).
- 27) K. Katayama, K. Hasegawa, H. Osawa, T. Akiba and H. Yanagida, *Sens. Mater.*, **2**, 57-66 (1990).
- 28) M. Guglielmi, P. Colombo, L. Degli Esposti and G. Mancinelli, *J. Mater. Sci.*, **27**, 5052-56 (1992).
- 29) The SADTLER Standard Spectra, SADTLER Lab. Inc., Y249K (1967).
- 30) J. Cheng and D. Wang, *J. Non-Cryst. Solids*, **100**, 288-91 (1988).
- 31) D. Bersani, P. P. Lottici, M. Braghini and A. Montenero, *Phys. Stat. Sol. (b)*, **170**, k5-k10 (1992).
- 32) C. D. Wagner, "Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy", Ed. by D. Briggs and M. P. Seah, Wiley, London (1983) App. 4.
- 33) P. Swift, D. Shuttleworth and M. P. Seah, "Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy", Ed. by D. Briggs and M. P. Seah, Wiley, London (1983) App. 2.
- 34) E. Paparazzo, J. L. Dormann and D. Fiorani, *Phys. Rev. B*, **28**, 1154-57 (1983).
- 35) E. McCafferty and A. C. Zettlemoyer, *Discuss. Faraday Soc.*, **52**, 239-63 (1971).
- 36) J. H. Anderson and G. A. Parks, *J. Phys. Chem.*, **72**, 3362-68 (1968).
- 37) G. Gusmano, G. Montesperelli, E. Traversa and A. Bearzotti, *Sens. Actuators B*, **B14**, 525-27 (1993).
- 38) G. Gusmano, G. Montesperelli, P. Nunziante and E. Traversa, *Br. Ceram. Trans. J.* (1993) in press.