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Electrical Humidity Response of Sol–Gel Processed Undoped and Alkali-doped TiO_2–Al_2O_3 Thin Films

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Abstract

Al_2O_3-TiO_2 thin films were prepared by a sol–gel processing. Sols were prepared having different TiO_2/Al_2O_3 molar ratios, i.e., 9:1, 8:2, and 6:4, without and with the addition of 10 at% of K ions. The films were prepared by dipping the substrates (silicon wafers, alkali-free glass or alumina with comb-type Au electrodes) in the sols. The films were fired in air for 1 h at 300, 500, 650 and 800°C. The films were amorphous, at any composition, up to the firing temperature of 500°C. Crystallization of the films was inhibited by larger contents of Al_2O_3 and K. The humidity-sensitive electrical properties of the thin films were studied using d.c. and a.c. measurements. The addition of K dramatically improved the relative humidity response of the films.

Keywords: sol-gel processes, films, electrical properties, TiO_2, Al_2O_3

1 Introduction

The currently available commercial humidity sensors are mainly based on polymeric films, even though ceramic oxides possess superior properties insofar as chemical resistance and mechanical strength are considered.[1] The main reasons for the present success of polymer-based humidity sensors are their low cost and the need for a heat-cleaning treatment of the ceramic sensors.[2] The latter is necessary to recover the performance of the ceramic sensors from drift in resistance, due to the gradual formation of stable chemisorbed OH^- on the oxide surface for exposure to humid environments.[3] The drift is related to the protonic-type humidity sensing mechanism for porous oxides at room temperature.[4]

Recently, there is a great effort to study ceramics in film form for humidity sensors, for the aim of fabrication of integrated sensors.[5] Some of the authors of this paper have studied the performance of various materials prepared by sputtering[6,7] or by sol–gel methods.[8–12] The sol–gel processing offers an economical technique for the deposition of ceramic films, which can be competitive with polymer film production, because it allows the direct preparation of films by dip- or spin-coating.[13]

Very large humidity response has been recently found for sol–gel processed TiO_2 thin films doped with 10 at% K or Li.[14] Although the films were dense, resistance versus relative humidity (RH) showed variations as high as 8 orders of magnitude in the RH range tested. These films showed good stability over time, with a limited drift.[15] These novel results were attributed to a conduction mechanism which involves the charge transport by alkali ions in the bulk of the film, greatly enhanced by RH.[16] The improvement in the performance of these ceramic sensors can be in fact attributed to their recently proposed humidity sensing mechanism.[17]

In this paper, we report results about the humidity sensitive electrical properties of sol–gel processed thin films based on TiO_2–Al_2O_3. Several films were prepared with the addition of alkali in order to check whether their influence was similar to what observed for the titania-based films.

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2 Experimental Procedure

A sol (S1) containing aluminum 3-sec butoxide [$Al(OBu^t)_3$, Aldrich], with acetylacetone (AcA, Aldrich) as a chelating agent and ethanol (EtOH, Prolabo) as a solvent, was refluxed at 80°C for 1 h. The molar ratios of the components were: $Al(OBu^t)_3$:AcA:EtOH = 1:1:60.

Another sol (S2) was prepared, containing titanium butoxide [$Ti(OBu^t)_4$, Aldrich], AcA as a chelating agent, bidistilled water for hydrolysis, HNO_3 as a catalyst, and EtOH as a solvent. The sol was left to react under stirring at 60°C for 3 h. The molar ratios were: $Ti(OBu^t)_4$:AcA:HNO_3:H_2O:EtOH = 1:0·5:0·01:2:28.

After their preparation, S1 and S2 were mixed together and stirred for 30 min at 25°C. Three different sols were obtained by mixing S1 and S2 in the proper amounts to give the molar ratios: $TiO_2/Al_2O_3 = 90:10$ (samples T9A1), $TiO_2/Al_2O_3 = 80:20$ (samples T8A2), $TiO_2/Al_2O_3 = 60:40$ (samples T6A4).

K-doped samples were prepared by adding $C_2H_3KO_2$ (Prolabo) to the T9A1, T8A2, and T6A4 sols, in such amounts to give a concentration of 5 at% or 10 at% of K^+ ions with respect to the Al and Ti atoms. After the addition of $C_2H_3KO_2$, the sol was left to react under stirring for 1 h at 40°C.

Al_2O_3–TiO_2 films were deposited, from fresh sols without and with K-doping, by dip-coating in a humidity controlled box, with relative humidity lower than 30%. The scheme of the thin-film processing is reported in Fig. 1. Silicon wafers were used as substrates for the materials characterization, while for the electrical measurements the films were deposited on alkali-free glass or alumina substrates with comb-type gold electrodes. The samples were introduced directly in the furnace after deposition and fired in air for 1 h at 300, 500, 650 and 800°C.

Powders were obtained from solutions poured into Petri dishes and maintained in a thermostatic chamber for 1 day at 60°C. Differential thermal analysis (DTA) was carried out on powder samples at a heating rate of 10°C/min in air by a STA 409/429 Netzsch analyser.

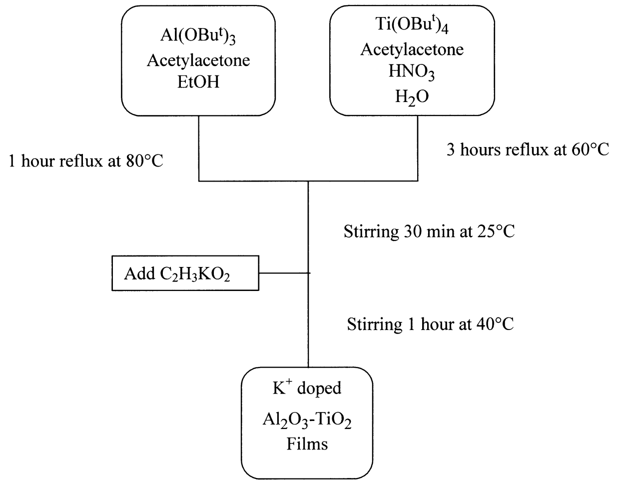

Fig. 1. Flow chart of the preparation of K-doped Al_2O_3–TiO_2 thin-films.

The coating thickness was measured with a profilometer (Alpha Step 200, Tencor Instrument) on a step made by scratching the film after the deposition. X-ray diffraction analysis (XRD) was performed on the films deposited on silicon substrates by a Philips PW 1740 diffractometer with a glancing angle technique. Cu kα, operating at 40 kV and 50 mA, was used as the radiation source. The morphology of the films was observed using scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360).

The electrical properties of the films were analysed by d.c. and a.c. measurements at different relative humidity (RH) values ranging from 4 to 90%, obtained by mixing controlled flows of dry and water-saturated air. Monitoring of RH within the test chamber was performed using a commercial sensor (Phys-chem, mod. PCRC-11). The d. c. measurements were performed using a Keithley quasistatic CV-meter 595. Current measurements upon application of 10 V d.c. were carried out cycling RH, in order to evaluate the response time of the sensors and their reproducibility. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10^{-2} to 10^5 Hz, using a Solartron 1255 frequency response analyser (FRA). In order to increase the input impedance of the apparatus up to 10^{12} Ω the FRA was coupled with an impedance adaptor built by us. All the measurements were performed at the controlled temperature of 40°C.

3 Results and Discussion

3.1 Materials characterization

Figure 2 shows the DTA curves of the K-doped T9A1, T8A2 and T6A4 powders. The DTA curves of all the three samples showed a broad endothermic effect around 100–200°C, due to the evaporation of residual water and alcohol, followed by a wide exothermic peak, in the range 250–550°C, which was accompanied by another peak with its maximum at 600°C for the T6A4 sample [Fig. 2(c)]. This complex exothermic peak was formed by the overlapping of two effects, the combustion of the unreacted organic groups of the alkoxides and the slow crystallization of TiO_2 in the anatase structure, as confirmed by XRD measurements. At temperatures above 650°C, it is not possible to clearly distinguish other peaks, while for the undoped samples two exothermic peaks, whose position shifted towards higher temperatures with increasing the Al_2O_3 content, were observed.[18] These peaks were attributed to the crystallization of titania in the rutile phase for the first one, and to the crystallization of α-Al_2O_3 for the second one.

SEM observations showed that all the films were continuous and free of features, when they were fired at temperatures lower than 650°C. Above this temperature, grains started to be formed, without the presence of pores.

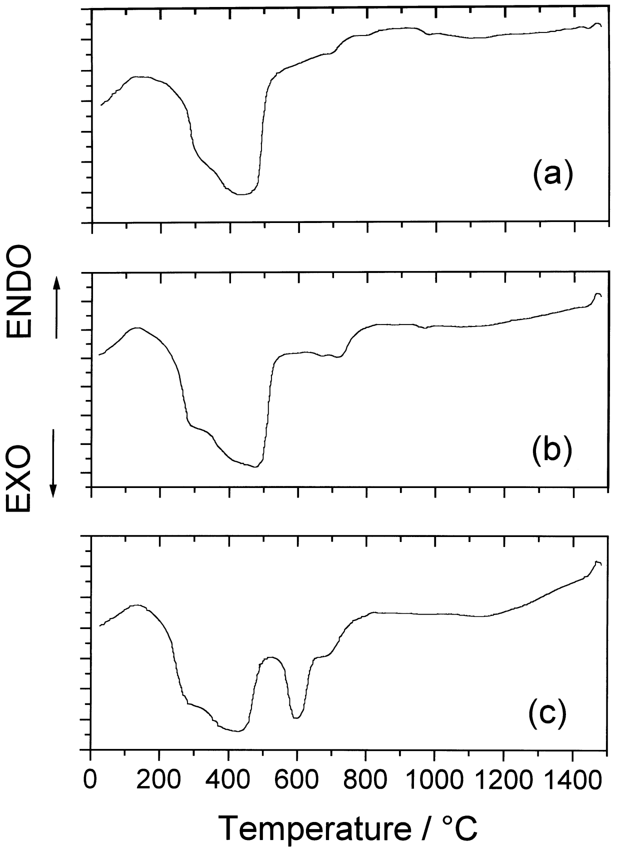

Fig. 2. DTA curves of the K-doped $A1_2O_3$–TiO_2 powders: (a) T9A1; (b)T8A2; (c) T6A4.

Figure 3 shows the XRD patterns of the K-doped alumina–titania films after firing at 650 and 800°C for 1 h in air. The measured thickness of all the films prepared was in the range from 100 to 150 nm. All the samples annealed at 300 and 500°C (not shown in Fig. 3) were amorphous. At 650°C, the peaks of TiO_2 in the anatase crystal structure at $2\theta = 25{\cdot}3°$ (100) and $2\theta = 48°$ (200) were detected for the T9A1 [Fig. 3(f)] and T8A2 [Fig. 3(d)], while the T6A4 film remained amorphous [Fig. 3(b)]. At 800°C, the intensity of the anatase peaks increased with increasing the temperature for the T6A4 [Fig. 3(a)] and the T8A2 [Fig. 3(c)] films, while for the T9A1 film [Fig. 3(e)] the intensity of the anatase peaks decreased and the peak corresponding to the (110) orientation of titania in the rutile structure was observed.

For the undoped $A1_2O_3$–TiO_2 films, we have reported that the presence of larger contents of Al_2O_3 has an inhibitory effect on the crystallization of titania in both anatase and rutile structures.[18] This is confirmed also for the K-doped Al_2O_3–TiO_2 thin-films, in agreement also with the DTA measurements. The addition of K seems to further inhibit the material crystallization, as shown both by XRD and DTA analysis. In fact, the formation of crystalline metastable pseudobrookite β-Al_2TiO_5, which was observed for the undoped films,[18] did not take place upon K addition.

3.2 Humidity-sensitive electrical measurements

Figure 4 shows the RH dependence of d.c. for the undoped and 10 at% K-doped T9A1 thin-films fired at 300°C. The addition of K dramatically improved the humidity response of the films; while the undoped film was almost insensitive to RH, the current versus RH variation for the K-doped T9A1

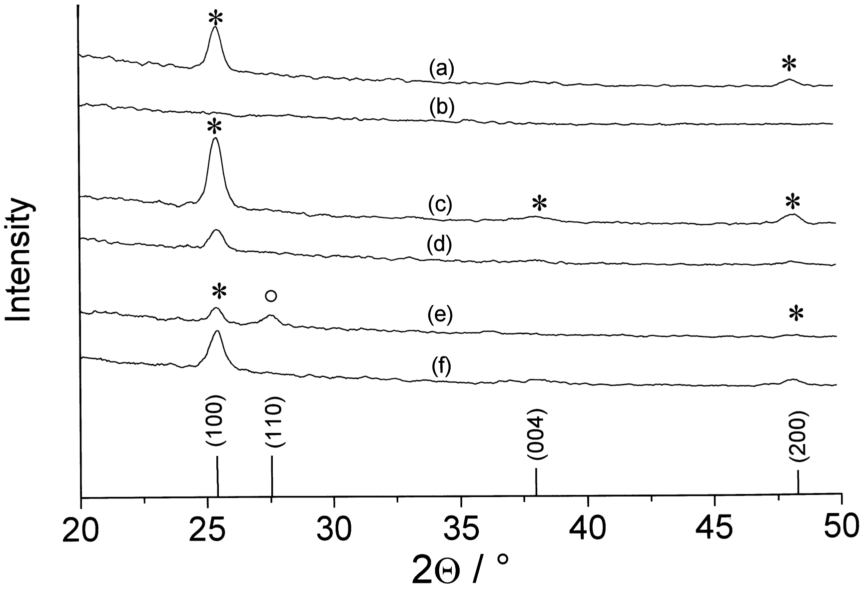

Fig. 3. XRD patterns of the K-doped Al_2O_3–TiO_2 thin-films deposited on silicon and annealed for 1 h in air: (a) T6A4, 800°C; (b) T6A4, 650°C; (c) T8A2, 800°C; (d) T8A2, 650°C; (e) T9AI, 800°C; (f) T9A1, 650°C (* anatase TiO_2; o rutile TiO_2).

film was of 5 orders of magnitude in the whole RH range tested.

Figure 5 shows the comparison between the RH dependence of d.c. for the various 10 at% K-doped thin-films fired at 300°C. The trend of the dependence of the RH response with the alumina content was not clear. The best response was shown by the T9A1 film, which showed also a lower intrinsic resistance. The T8A2 film showed a larger RH response at RH values higher than 60%, while for the T6A4 film, which showed a current variation of almost 5 orders of magnitude in the whole RH range, the response was larger at intermediate RH values.

The same trend of RH response with Al_2O_3 was observed also for the K-doped films fired at 500°C, with a general reduction of the response for all the alumina contents. As an example, the current versus RH variation for the K-doped T9A1 film fired at 500°C became of 4 orders of magnitude in the whole RH range tested.

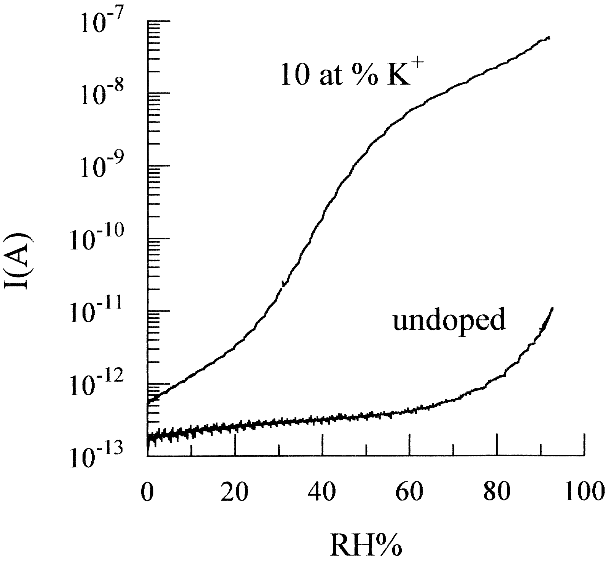

Fig. 4. The RH dependence of the current for the undoped and 10 at% K-doped T9A1 thin-films fired at 300°C, measured with 10 V d.c. at 40°C.

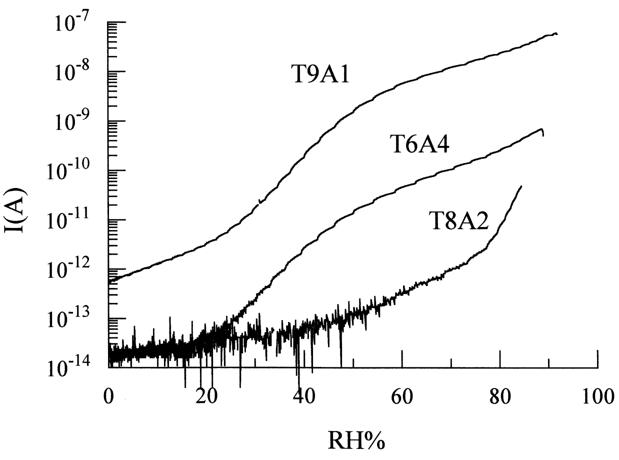

Fig. 5. The RH dependence of the current for the 10 at% K-doped T9A1,T8A2, and T6A4 thin-films fired at 300°C, measured with 10 V d.c. at 40°C.

The complex impedance plane plots recorded for the undoped films heated to 300°C and 500°C were almost not affected by humidity; at all the RH values tested, the EIS plots showed a single semicircle which was slightly inclined to the real axis. The larger the RH, the smaller the impedance of the films. As it is well known,[19] a semicircle on the complex impedance plane plot is due to a resistive and a capacitive element in parallel. For these films, the equivalent electrical circuit can be described by a parallel RC element, corresponding to the contribution of the grain surface.[20]

A different behaviour was observed for the K-doped films. At low RH values, a single semicircle was observed, which decomposed in two semicircles at higher RH values. As an example, Fig. 6 shows the complex impedance plots measured at 60, 70 and 80% RH for the 10 at% K-doped T9A1 film fired at 500°C. The frequency at which occurred the relaxation of the RC element increased with increasing RH.

For the K-doped films, the element at high frequencies can be ascribed to the grain surface and/or bulk. The semicircle at low frequencies was due to polarization effect at the electrode–electrolyte interface. The electrodes used are made of Au, which is an electronic conductor. At low frequencies, there is a charge build-up at the blocking metal electrodes, because the charge carriers are ions. The excess charge at the electrodes causes a polarization effect which increases with increasing RH.

The resistance (R) values, calculated from the intercepts of the high-frequency semiarc of the spectra with the real axis on the complex impedance plane plots, decreased with increasing RH, while no significant changes with RH were observed for the capacitance (C) values, evaluated at the frequency of the maximum of the semicircle in the complex impedance plane plots. These findings were in agreement with those previously observed for the K-doped titania films.[16] The ionic-type sensing

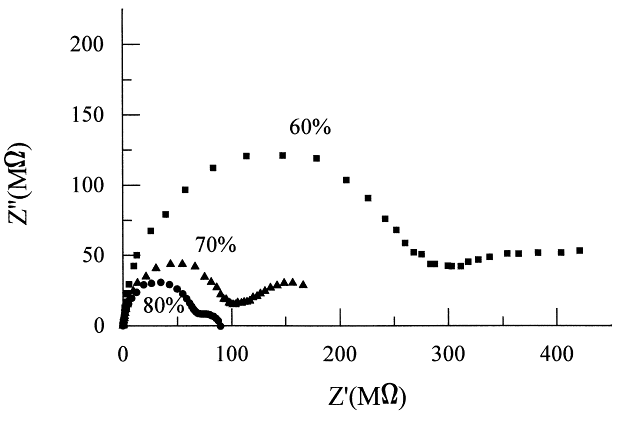

Fig. 6. Complex impedance spectra of the 10 at% K-doped T9A1 thin-film fired at 500°C, measured at 40°C at various RH values.

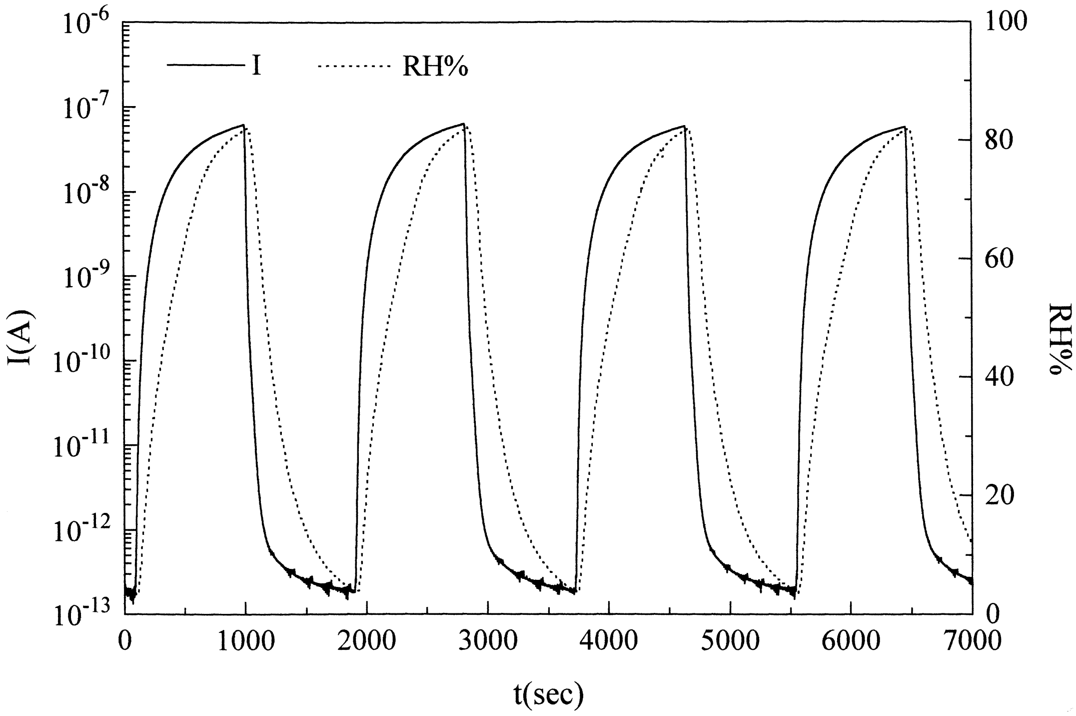

Fig. 7. Current response to cyclic RH variations of the 10 at% K-doped T9A1 thin-film fired at 300°C, measured with 10 V d.c. at 40°C, reported with the response of the reference RH sensor.

mechanism cannot explain the large RH response of these thin films. The sensing mechanism is probably similar to that of alkali-doped titania films, with a contribution of alkali ions as charge carriers.[16] The water adsorbed on film surface enhances ionic conductivity in the film for the alkali-doped materials, likely due to the mobility of K^+ ions.

Figure 7 shows the response time of the 10 at% K-doped T9A1 thin-film fired at 300°C. The results were rather reproducible. The response time of the film was slightly smaller during desorption than during water adsorption. The response of the tested film was faster than the response of the commercial sensor, which is very promising for their practical application. This means that even though charge carriers are supposed to be K ions, their mobility is rather fast.

4 Conclusions

Good quality Al_2O_3–TiO_2 thin films with different molar ratios were prepared using a sol–gel technology, without and with addition of K. The K-doped films showed promising performance as humidity sensors having a novel sensing mechanism. The addition of K is important for the improvement of the humidity sensing characteristics.

Acknowledgements

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