POROUS THIN FILM HUMIDITY SENSOR BASED ON DOPED AND UNDOPED TITANIA

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Key words: humidity sensors, TiO_2, titanium dioxide, thin films, potassium doped TiO_2 titanium dioxide, undoped TiO_2 titanium dioxide, porous materials, electrical properties

Abstract: Potassium doped and undoped TiO_2 thin films were prepared by the sol-gel technique. The influence of potassium addition and of the film firing temperature on the sample morphology, and on the electrical properties of TiO_2 thin films were studied. The effect of introducing pores in undoped and potassium doped TiO_2 thin films on their humidity sensing characteristics was also studied. Introduction of the porosity in thin films had a positive effect on the humidity sensing characteristics of the samples. Sol-gel processed, porous, and 10 at. % potassium doped TiO_2 thin films heated to 450°C exhibited an outstanding humidity sensitivity over the entire RH range.

Senzor vlage na osnovi poroznega dopiranega in nedopiranega TiO_2

Ključne besede: senzorji vlage,TiO_2 dioksid titanov, plasti tanke, TiO_2 dioksid titanov dopiran s kalijem, TiO_2 dioksid titanov nedopiran, materiali porozni, lastnosti električne

Povzetek: S sol gel tehniko so bile pripravljene s kalijem dopirane in nedopirane TiO_2 tanke plasti. Študirali smo vpliv kalija in temperature žganja tanke plasti na morfologijo in električne lastnosti plasti. Preiskovali smo tudi vpliv poroznosti tankega filma na senzorske lastnosti. Poroznost filma ima pozitivni efekt na lastnosti senzorja vlage. Senzor vlage pripravljen iz poroznega TiO_2 filma dopiranega s 10 at.% kalija ima po žganju pri 450°C zelo dober odziv v celotnem področju vlažnosti.

Introduction

Today, most commercially available humidity sensors are based on polymeric films, in spite of the fact that ceramic humidity sensors exhibit better chemical resistance and mechanical strength than polymeric sensors /1/. This situation is a consequence of the high costs that are incurred during the production of ceramic humidity sensors based on porous sintered oxides /2, 3/, because of the use of conventional ceramic technology. For that reason less costly manufacturing technology for miniature ceramic sensing elements is needed. Recently, films prepared by sol-gel methods were studied /4, 5/ as humidity sensing devices. This chemical technique offers a very promising feature, namely, the possibility of powder-free processing of ceramics in their final shape (films or fibres), which can be used as active elements in sensing devices /6/.

That is probably one of the reasons that several authors studied the suitability of sol-gel processed TiO_2-based thin films for humidity sensors /4, 5, 7, 8/. Titania was used as a sensing material because very interesting results have been reported for sintered porous compacts and thick films of titania and doped titania-based humidity sensors /9, 10, 11/. In the literature it was considered that a large pore volume and control of the pore size distribution are necessary for high humidity sensitivity of ceramic materials /3, 12/. For this reason it is interesting that an outstanding humidity sensitivity over the entire RH (relative humidity) range has been reported in dense, pore-free thin films/8/. Such a high response of sol-gel processed K-doped TiO_2 films has also rarely been observed for porous sintered ceramics. It is known that addition of alkali ions is effective in increasing the RH sensitivity of several ceramic oxides by affecting the sinterability of the material in pellet form /10/, decreasing the intrinsic resistance of the material /13/, or increasing the number of adsorption sites /14/. However, measurements performed by the authors /4, 8/ indicated a humidity sensing mechanism that is different from that generally accepted for porous ceramics This mechanism involves the direct participation of alkali ions in conduction during the exposure of the sensing material to a humid environment /4/.

In this study the influence of the introduction of pores in undoped and potassium doped TiO_2 thin film on their sensing characteristics is studied. Potassium ethoxide was used for introduction of potassium ions to the sols. The influence of potassium compound and pore former on the morphology and on the electrical properties of TiO_2 thin films were studied.

Experimental

TiO_2 thin films were prepared by the sol-gel technique. Precursor solutions for production of porous TiO_2 coatings were prepared by a slightly modified method reported by Kato et al. /15, 16/. Titanium tetraisopropoxide (TTIP) (Alfa Products), diethanolamine (Alfa Products), and ethanol (Carlo Erba) were mixed and stirred in a nitrogen glove box to prepare a homogenous solution. For preparation of doped TiO_2 films 10 at % of K was added to the solution. Sols were doped with potassium ethoxide (Alfa Products). Afterwards water diluted with ethanol was mixed into the solution. The water/alkoxide molar ratio was 1.

Polyethylene glycol (PEG) (Aldrich), molecular weight 1800-2200, was used as a pore former /15/ in several samples. In order to evaluate the influence of the concentration of the pore former on the porosity, the amount of PEG was varied between 2 and 4 wt. %. In the text we will use following notation: KE/Px.x - samples prepared with potassium dopant added, NK/Px.x -

samples prepared without potassium dopant added. In the notation Px.x represents the wt. % of PEG added.

Silicon wafers and alumina plates were used as support substrates. For electrical measurements, prototype sensors were prepared by depositing TiO_2-based films on alumina substrates with comb-type Au electrodes. The films were deposited from the solutions by the spin coating technique, using a rotation speed of 3000 RPM. Gel coatings were dried at 100°C and fired at 650°C for 1 hour /15/. Samples were also fired at 450°C for 2 hours in order to evaluate the influence of firing temperature on the sensing characteristics of TiO_2 thin films. The thickness of the TiO_2 coating was increased by repeating the cycle from spinning to firing.

The morphology and topography of the coatings was examined by scanning electron microscopy (SEM, JEOL JXA-840A) and scanning probe microscope (SPM, Digital Instruments Nanoscope III). Generaly, SPMs are best suited for imaging relatively flat samples. Its depth of field is limited by the travel limits of the scanning tube and by tip size and geometry. For that reason real values for pores depth can be greater than observed values. Topography of the sample is represented by different contrast. Contrast bar on the left side of the SPM images links the contrast with the surface height of the sample.

The humidity sensitive electrical properties of the thin films were evaluated using an impedance analyser (HP 4192A LF). An environment varying relative humidity (RH), ranging from 15 to 95 % at 25°C was obtained using an environmental chamber (Weiss SB1 160).

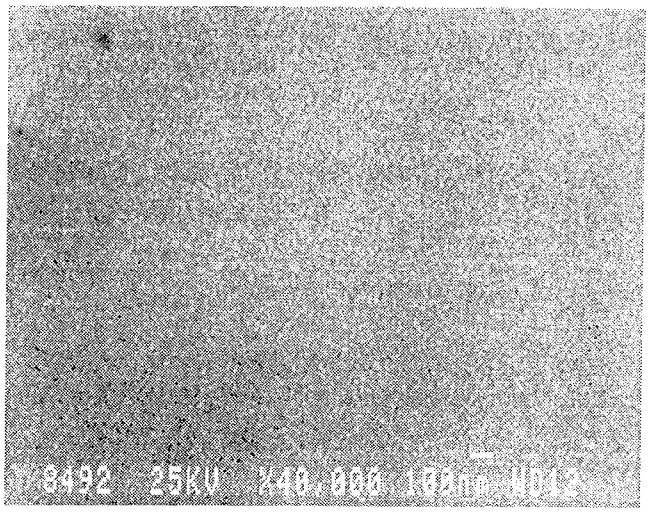
Results and discussion

The TiO_2 coating prepared from the solution without addition of polyethylene glycol (NK/P0.0) had almost no visible texture after firing at 450°C and 650°C (Fig. 1A). Firing of TiO_2 coating that was prepared from undoped sols with 2.4 wt. % of PEG added, at 650°C yielded thin films (NK/P2.4) with a porous microstructure (Fig. 1 B and C). Pores were from 100 nm to approximately 270 nm wide and at least 110 nm deep (Fig 1 C). There was almost no difference between microstructures of the samples NK/P2.4 fired at 450°C and 650°C.

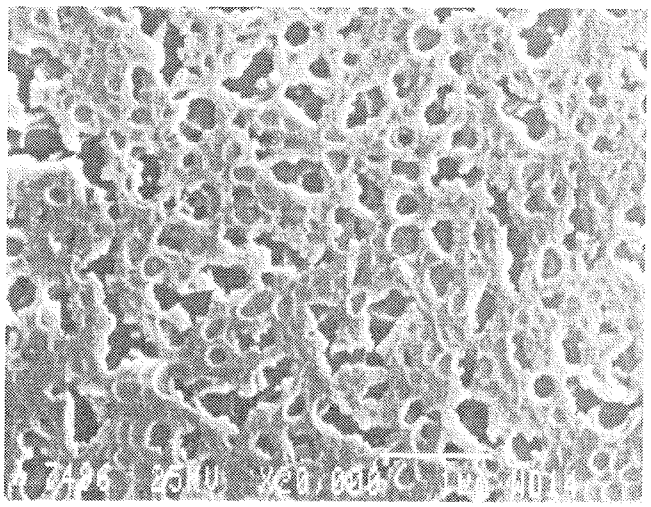
The influence of the addition of potassium compounds to the TTIP sol on the microstructure of the TiO_2 thin film is presented in Fig. 2 and 3.

Fig 2 show the morphology of K doped TiO_2 thin films fired at 650°C for 1 hour. There was slight difference between the morphology of KE/P0.0 (Fig. 2A and 2C) and the morphology of the KE/P4.0 sample (Fig. 2B and 2D). The sample without PEG added (KE/P0.0) had a granular microstructure with grains approximately 80 nm in diameter. Pores in Fig 2 C were from 10-50 nm wide and from 5 to ~15 nm deep. The sample KE/P4.0 with PEG added (Fig. 2D) had a microstructure with grains approximately 100 nm in diameter and pores ~50 nm wide and ~30 nm deep.

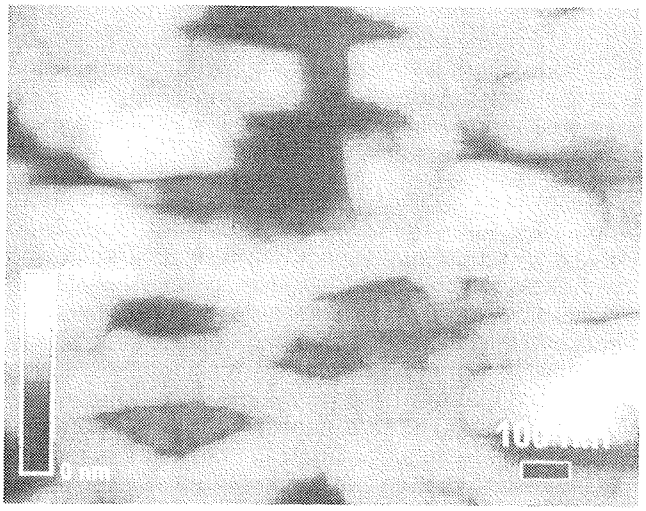
KE/P0.0 samples had also some areas with different contrast (Fig 2A). Areas with different contrast could also be observed in samples where the PEG concen-



A



B



C

Fig 1. Morphology of undoped TiO_2 thin films fired at 650°C for 1 h.
A. NK/P0.0 (SEM image),
B. NK/P2.4 (SEM image),
C. NK/P2.4 (SPM image)

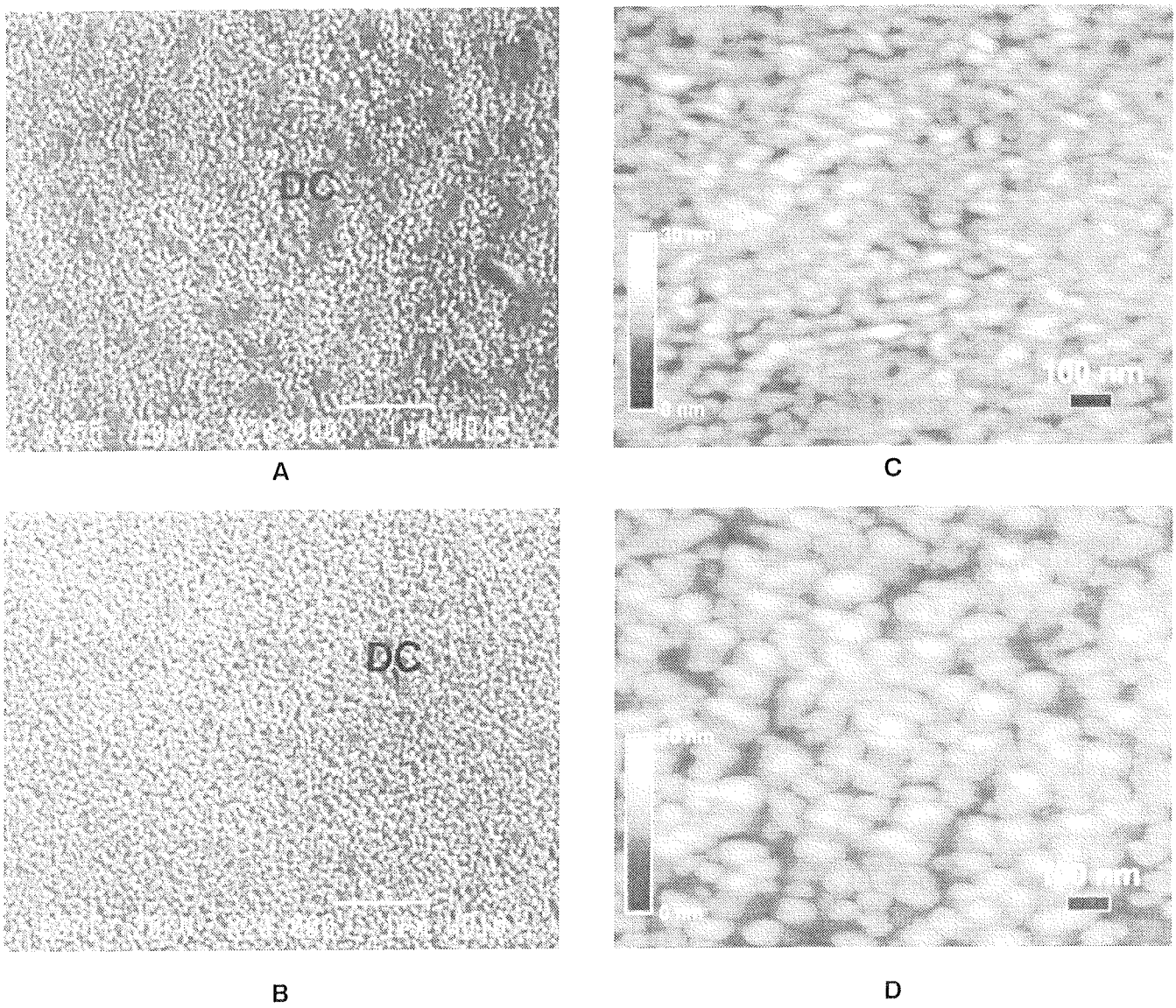


Fig 2. Morphology of potassium doped TiO_2 thin films fired at 650°C for 1 h. Samples were prepared from KOC_2H_5 doped sols.
A. KE/P0.0 (SEM image), B. KE/P4.0 (SEM image),C. KE/P0.0 (SPM image), D. KE/P4.0 (SPM image)

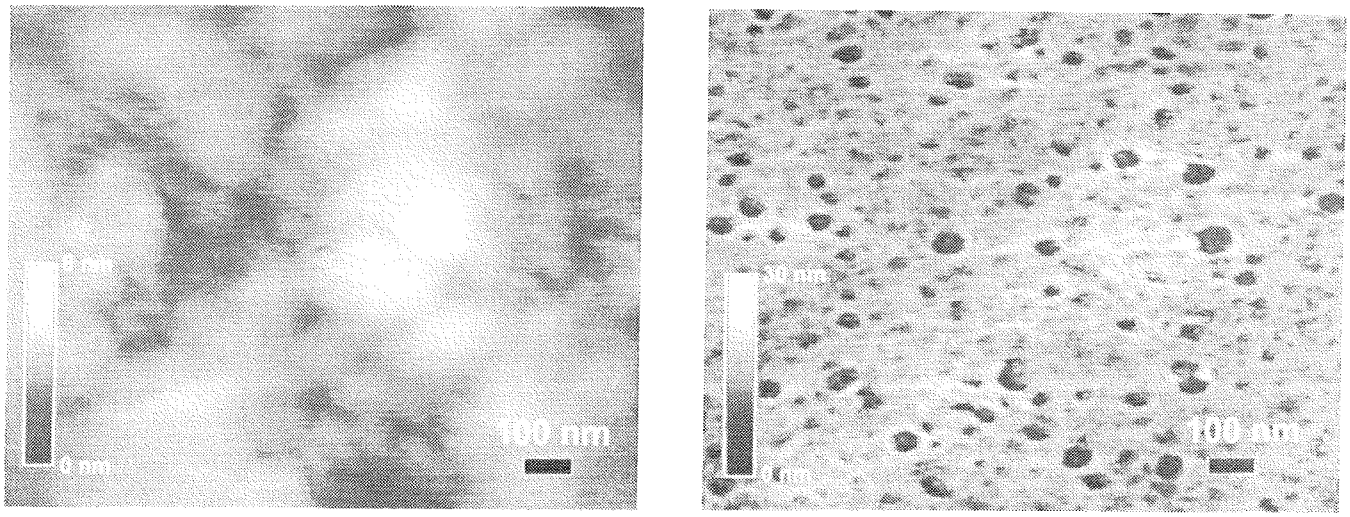
tration was increased to 4.0 wt. % (sample KE/P4.0 at Fig 2B), but their visibility was worse. EDX analysis revealed that concentration of K ions is higher in areas of different contrast (DC) than in the rest of the coating.

It is interesting that in spite of the fact that the PEG concentration in KE/P4.0 samples (Fig. 2B) was higher than in potassium undoped (NK/P2.4) samples (Fig 1B and 1C), no pores with higher diameter developed. The microstructure was still similar to the microstructure of the KE/P0.0 sample in Fig 2A.

It can be seen from these results that introduction of potassium compounds into the TTIP sols had a profound effect on the sample morphology. First, the formation of the pores in the samples with added potassium precursors was hindered with respect to the samples without K added. Second, the potassium doped samples fired at 650°C always exhibited the granular morphology whereas the undoped samples fired at same temperature (Fig.1A) had almost no granular texture.

Samples KE/P0.0 and KE/P4.0 fired at 450°C for 2 hours are presented in Fig 3A and B, respectively. TiO_2 thin films without added pore former (KE/P0.0) had no visible texture (Fig 3A). Topography of the sample varied in the range of 8 nm. TiO_2 coatings prepared from the precursor solution with PEG added (sample KE/P4.0) developed a different microstructure. As can be seen from the SPM micrograph in Fig 3B, there were pores in the coating. The pores were up to ~80 nanometres wide and ~20 nm deep. Segregation of potassium was not observed in these samples.

Dependence of the capacitance versus relative humidity for undoped TiO_2 thin films measured at 200 Hz and 25°C is presented in Fig 4. Samples NK/P2.4 and NK/P0.0, fired at 650°C for 1 hour, exhibit a change of capacitance only at high RH. There is almost no differ-



A B

Fig 3. Morphology of KE/P0.0 and KE/P4.0 samples fired at 450°C for 2h. A. KE/P0.0 (SPM image), B. KE/P4.0 (SPM image)

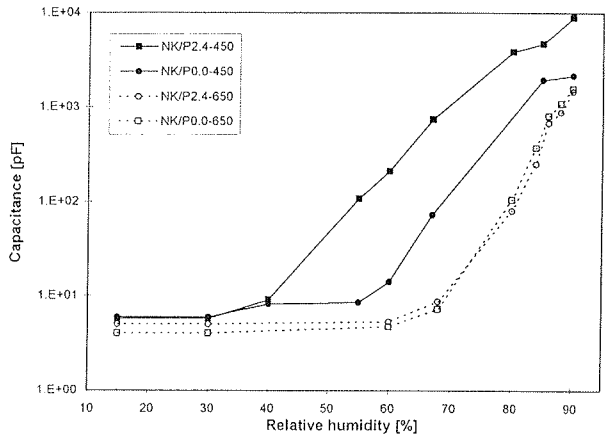


Fig 4. Dependence of capacitance vs. relative humidity for undoped thin films at 25°C. Sensors were fired at 650°C for 1h and at 450°C for 2h. The frequency of the applied field was 200 Hz.

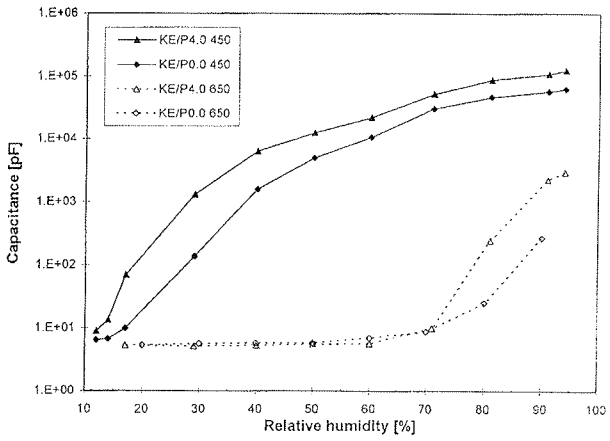


Fig 5. Dependence of capacitance vs. relative humidity for K doped thin films at 25°C. Sensors were fired at 650°C for 1h and at 450°C for 2h. The frequency of the applied field was 200 Hz.

ence between the samples. Thin films fired at 450°C exhibit higher sensitivity. The sensitivity of the samples with addition of pore former (sample NK/P2.4) is approximately for one order of magnitude higher than the sensitivity of NK/P0.0 sample. Dependence of the capacitance versus relative humidity for potassium doped TiO_2 thin films are presented in Fig 5 Samples KE/P0.0 and KE/P4.0, fired at 650°C for 1 hour, exhibit a change of capacitance only at high RH. The sensitivity of the samples to change of RH increased with addition of pore former (sample KE/P4.0) only for a relative humidity over 70 %.

The capacitance change for samples KE/P0.0 and KE/P4.0 fired at 450°C was 4 orders of magnitude between 15 and 90 % RH. Sample prepared from precursors with an increased concentration of PEG (KE/P4.0) had higher sensitivity in the range from 15 to 45 % RH than the KE/P0.0 sample. From 45 % RH, sensitivity of the KE/P4.0 sample decreased, and in the range from 50 to 95 % RH followed the sensitivity of the KE/P0.0 sample at higher capacitance level.

Frequency dependence of capacitance versus relative humidity for KE/P4.0 sample that was fired at 450°C, is presented in Fig 6 It can be seen that in the region from 15% RH to 60 % RH a sensitivity of KE/P4.0 sample decreases with increasing frequency of applied field.

On the one hand, the dramatic increase of sensitivity with decreased firing temperature could be explained by a coarsening of the microstructure at 650°C. At that temperature grains of TiO_2 are already well formed. Grains are also connected with necks (Fig 2C and 2D), in contrast to the sample films fired at 450°C which show

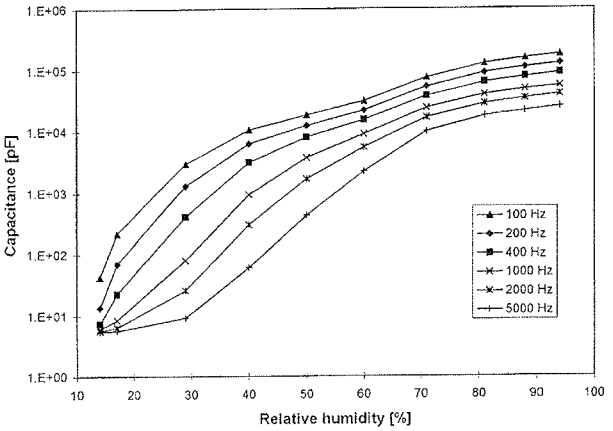


Fig 6. Dependence of capacitance vs. relative humidity for K doped thin films at 25°C measured at frequencies between 100Hz and 5000 Hz. Sensors were fired at 650°C for 1h and at 450°C for 2h

no grain morphology (Fig 3). It has been shown that formation of grain boundaries and ordering of the crystalline structure is able to block ionic conduction within the material /4, 5/. The authors /4/ showed that the free movement of alkali ions is necessary for exceptional conductivity of K doped TiO_2 thin films. The decrease of sensitivity could probably be also connected with the potassium segregation that can be observed in the samples fired at 650°C (Fig 2A and 2). Such segregation is not yet well understood, and further investigations are needed to explain it.

On the other hand, samples fired at 450°C show an exceptional change of capacitance in the entire RH range. This change could also be related to the increased number of water adsorption sites, due to the formation of a higher number of surface defect sites /2, 14/.

The presence of small pores in the KE/P4.0 sample fired at 450°C is probably responsible for the higher sensitivity of the thin film at lower relative humidity (below 45% RH) compared to the KE/P0.0 sample which was fired at the same temperature, and that has no visible porosity. Formation of grains and further coarsening of the sample microstructure (KE/P4.0) at 650°C probably resulted in the disappearance of the porosity that can be observed in Fig 3B. In any case, the porosity of the KE/P4.0 sample sintered at 650°C was still higher than the porosity of the KE/0.0 sample sintered at same temperature, and that probably resulted in higher sample sensitivity at a relative humidity over 70%RH.

Conclusions

Porous potassium doped and undoped TiO_2 thin films were prepared from alkoxide solutions by the spinning technique. The results showed that the formation of pores in the samples prepared from TTIP sols with potassium precursors added was hindered with respect to the samples prepared from TTIP sols without added potassium precursors.

Introduction of porosity in thin films had a positive effect on the humidity sensing characteristics of the potassium doped samples. Sol-gel processed, porous, and 10 at % potassium doped TiO_2 thin films heated to 450°C show an outstanding humidity sensitivity over the entire RH range. The change of capacitance was 4 orders of magnitude in the range from 15 to 95% RH.

Acknowledgments

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