THIN FILM HUMIDITY SENSOR BASED ON POROUS TITANIA

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Key words: humidity sensor, thin-film sensors, RH, Relative Humidity, TiO_2 porous titanium dioxide, electrical properties, sol-gel method, morphology

Abstract: The effect of introducing pores in undoped and potassium doped TiO_2 thin films on their humidity sensing characteristics was studied. Films were prepared by the sol-gel technique. Different potassium compounds were used to introduce potassium ions into the sols that were used for preparation of samples. The influence of these compounds and of the film firing temperature on sample morphology, and on the electrical properties of TiO_2 thin films were 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.

Tenkoplastni senzor vlage na osnovi poroznega titanovega dioksida

Ključne besede: senzorji vlage, senzorji tankoplastni, RH vlaga relativna, TiO_2 titanov dioksid porozni, lastnosti električne, postopki sol-gel, morfologija

Povzetek: V članku so predstavljeni senzorski elementi za zaznavanje relativne vlažnosti zraka na osnovi s kalijem dopiranih in nedopiranih TiO_2 tankih filmov. Predstavljen je tudi način, kako v tanek film lahko vpeljemo poroznost in kako le ta vpliva na njegove senzorske lastnosti. Filmi so bili pripravljeni s pomočjo sol-gel procesa. Različne kalijeve spojine so bile uporabljene kot dodatek k solom za pripravo tankih filmov. Študirali smo vpliv teh spojin in temperature žganja na morfologijo in električne lastnosti TiO_2 tankih filmov. S kalijem dopirani TiO_2 tanki filmi, ki so bili žgani pri 450°C in ki so bili pripravljeni s pomočjo sol-gel postopka, so imeli odlično občutljivost na spremembo relativne zračne vlage. Rezultati so pokazali, da poroznost pozitivno vpliva na občutljivost teh vzorcev.

Introduction

The trend towards automated control systems for environmental monitoring and miniaturisation requirements for on chip integration of sensors is the driving force for development of integrated humidity sensors /1, 2/. The final target is the development of intelligent system that will be easy to operate and have microprocessor-compatible read-outs. However, not only the electronics but also the materials technology is fundamentally important in improving research and development on humidity sensors. A complete understanding of the material's characteristics and of its sensing mechanism, using prototypes, is needed for the further development of advanced devices. In the field of humidity sensors, several attempts have been made to integrate a humidity sensor on silicon microchips, along with all electronics needed for a practical device. Both polymeric /3/ and ceramic films /4/ have been investigated as humidity sensitive elements.

Today, most commercially available humidity sensors are based on polymeric films /5/, in spite of the fact that ceramic humidity sensors exhibit better chemical resistance and mechanical strength than polymeric sensors / 6/. This situation is a consequence of the high costs that are incurred during the production of ceramic humidity sensors based on porous sintered oxides /1, 7/, 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 /8, 9/ 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 /10/.

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 / 8, 9, 11, 12/. 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 /13, 14, 15, 16, 17/. 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 /7, 18/. 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 /12/. 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 /15/, decreasing the intrinsic resistance of the material /19/, or increasing the number of adsorption sites /20/. However, measurements performed by the authors /8, 12/ 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 / 8/.

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. Different potassium compounds were used for introduction of potassium ions to the sols that were used for preparation of samples. The influence of these compounds on the morphology and on the electrical properties of TiO_2 thin films were also studied.

Experimental

Doped and undoped 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. /21, 22/. Titanium tetraisopropoxide $Ti(OPr^i)_4$, diethanolamine, and ethanol 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. Three different compounds were used for doping of the sols: potassium nitrate (KNO_3), potassium acetate ($KOOCCH_3$), or potassium ethoxide (KOC_2H_5). Afterwards water diluted with ethanol was mixed into the solution. The water/alkoxide molar ratio was 1.

Polyethylene glycol (PEG), molecular weight 1800-2200, was used as a pore former /21/ 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. %. A summary of the samples prepared is presented in Table 1.

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 /21/. 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 of the coatings was examined by scanning electron microscopy (SEM, JEOL JXA-840A). 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).

Table 1: Summary of prepared samples

	Pore former	
potassium dopant	PEG added	No PEG added
KNO_3	KN/Px.x*	KN
$KOOCCH_3$	KA/Px.x*	KA
KOC_2H_5	KE/Px.x*	KE
No K^+ added	NK/Px.x*	NK

x.x represents the wt. % of PEG added. Example: KN/P2.4, sample with KNO_3, and 2.4 wt. % of PEG added to the sol.

Results and discussion

Figs 1 and 2 show scanning electron micrographs of the undoped, and potassium doped TiO_2 coatings prepared from the precursor solutions.

The TiO_2 coating prepared from the solution without addition of polyethylene glycol (NK/P0.0, Fig.1A) had almost no visible texture. Addition of 2.4 wt. % of PEG to undoped titanium tetraisopropoxide (TTIP) sols yielded thin films (NK/P2.4) with a porous microstructure (Fig. 1B). Pores were from 100 to approximately 270 nm in diameter. The sample morphology was slightly different from the morphology of thin films reported in the literature /21/ but this difference can probably be ascribed to the different coating technique used.

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. The amount of potassium compound ($KOOCCH_3$, KNO_3) added was calculated to yield 10 at. % of potassium ions with respect to titanium ions.

Fig 2A show the morphology of a KA/P2.4 sample (potassium acetate and 2.4% of PEG added to the TTIP sol) fired at 650°C for 1 hour. There was no difference in morphology between samples without addition of PEG (KA/P0.0) and samples with 2.4 wt. % of PEG added (KA/P2.4). Both samples had microstructures almost identical to the fine granular microstructure of the sample KN/P0.0 (KNO_3 added, no PEG added) that were fired at 650°C for 1 hour. The samples had a grain size in the range from ~20 nm to ~100 nm (Fig 2A).

An increased concentration of pore former in the KNO_3 doped precursors (sample KN/P2.4) yielded a microstructure that is presented in Fig 2B. The sample had a grain size around 100 nm and pores in the range from ~20 nm to ~200 nm. Large cracks from 0.5 to 2 μm were also present in these samples. During the preparation of the KN/Px.x samples separation of small crystallites was observed. This was probably a consequence of the low solubility of KNO_3 in TTIP sols.

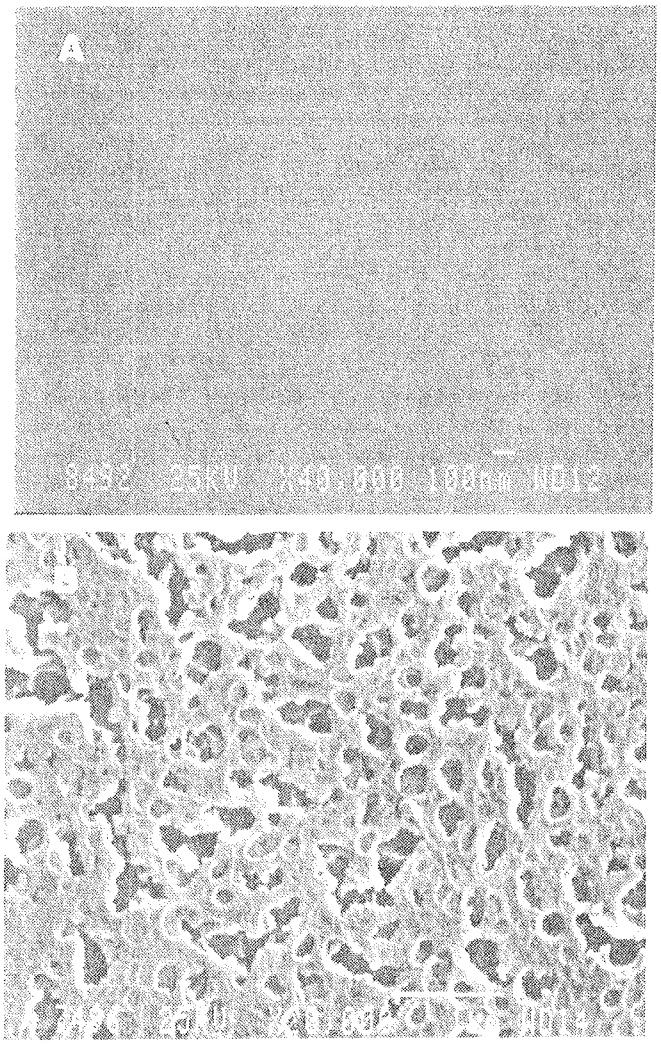

Fig. 1: Morphology of undoped TiO_2 thin films fired at 650°C for 1 h.
A: NK/P0.0, B. NK/P2.4

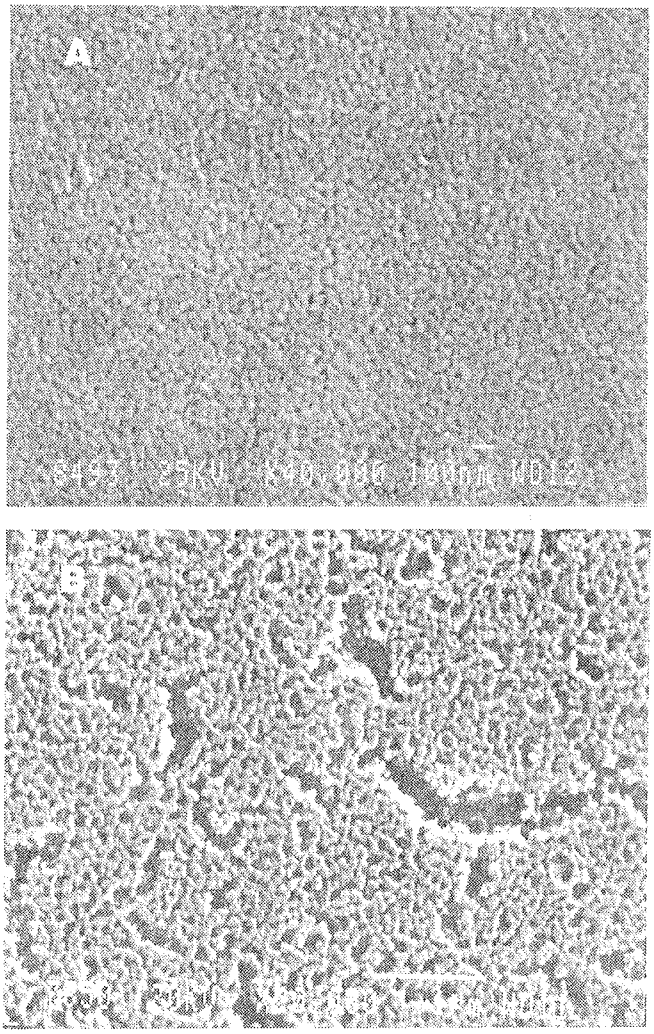

Fig. 2: Morphology of potassium doped TiO_2 thin films fired at 650°C for 1 h. Samples were prepared from $KOOCCH_3$ and KNO_3 doped sols.
A: KA/P2.4, B. KN/P2.4

Fig 3 show the morphology of K doped TiO_2 thin films fired at 650°C for 1 hour. Potassium ethoxide was used as precursor. The sample without PEG added (KE/P0.0) had a granular microstructure with ~100 nm grains and 10-50 nm pores (Fig 3A). There was no visible difference between the morphology of KE/P0.0 and the morphology of the KE/P2.4 sample. Both samples had some areas with larger grains and different contrast (Fig 3A). EDX analysis revealed that concentration of K ions is higher in areas of different contrast (DC) than in the rest of the coating.

Areas with different contrast could also be observed in samples where the PEG concentration was increased to 4.0 wt. % (sample KE/P4.0 at Fig 3B), but their visibility was worse. It is interesting that in spite of the fact that the PEG concentration in KE/P4.0 samples was higher than in potassium undoped (NK/P2.4) samples (Fig 1B), no pores with higher diameter developed. The microstructure was still similar to the microstructure of the KE/P0.0 sample in Fig 3A.

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. 1) had almost no granular texture.

Samples prepared from TTIP sols based on potassium ethoxide precursor, were selected to evaluate the influence of firing on the morphology and electrical properties of the thin films. Samples KE/P0.0 and KE/P4.0 were fired at 450°C for 2 hours (Fig 4). TiO_2 thin films without added pore former (KE/P0.0) had no visible texture (Fig 4A). 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 micrograph in Fig 4B, there were fine pores in the coating. The pores

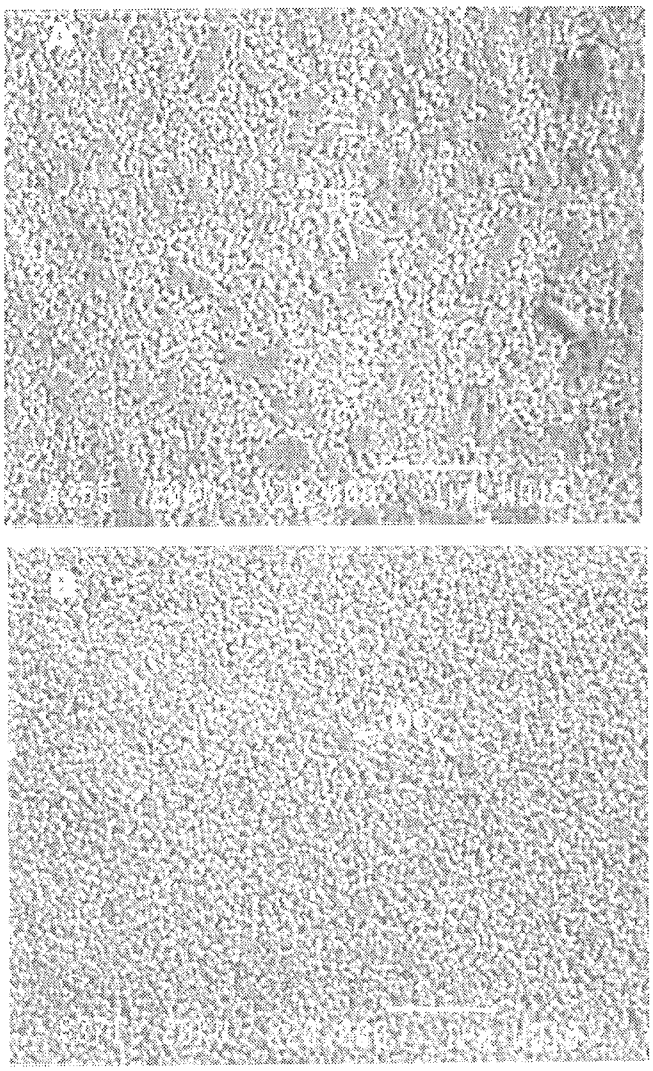

Fig. 3: Morphology of potassium doped TiO_2 thin films fired at 650 °C for 1 h. Samples were prepared from KOC_2H_5 doped sols. A. KE/P0.0, B. KE/P4.0

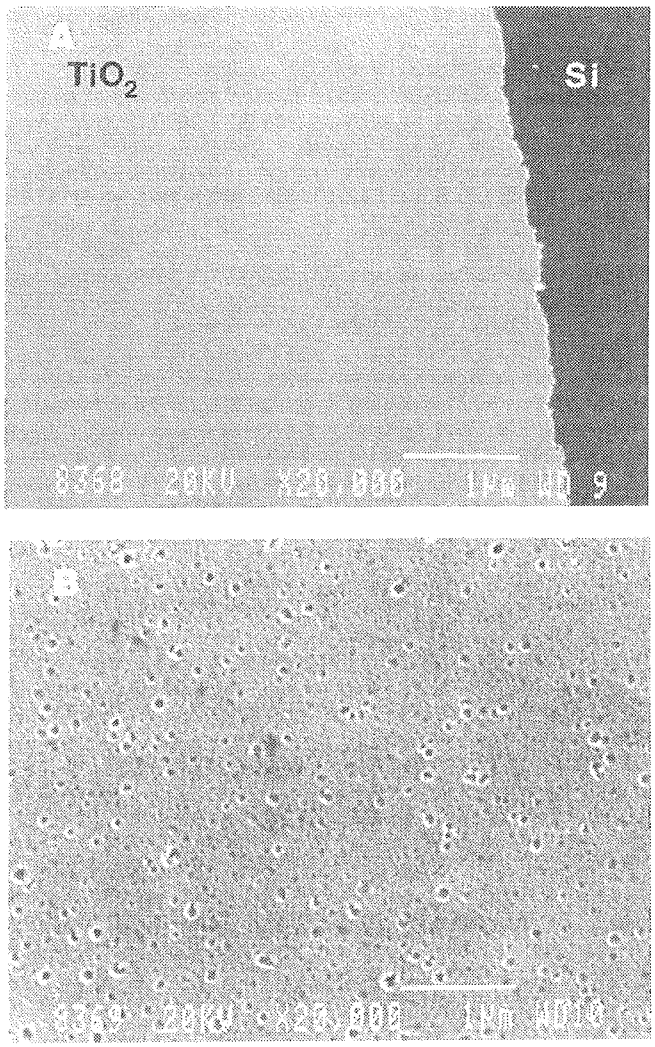

Fig. 4: Morphology of KE/P0.0 and KE/P4.0 samples fired at 450°C for 2 h. A. KE/P0.0, B. KE/P4.0

were ~30 to ~100 nanometres in diameter. No areas of different contrast could be observed in these samples.

Electrical measurements proved that potassium nitrate was unsuitable for sample doping due to the low solubility of KNO_3 in the TTIP sols. For this reason the potassium concentration in the TiO_2 thin films doped with this compound was under 10 at. % (with respect to Ti), and as a consequence /12, 15, 19, 20/ KN/P0.0 and KN/P2.4 samples were poorly sensitive to changes of relative humidity (RH).

Fig 5 show the dependence of the capacitance of potassium doped TiO_2 thin films at 200 Hz and 25°C. 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.

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 3), in contrast to the sample films fired at 450°C (Fig 4) which show no grain morphology in SEM observations. It has been shown that formation of grain boundaries and ordering of the crystalline structure is able to block ionic conduction within the material / 8, 9/. The authors /8/ 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 3). 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 /1, 20/.

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 4B. 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.

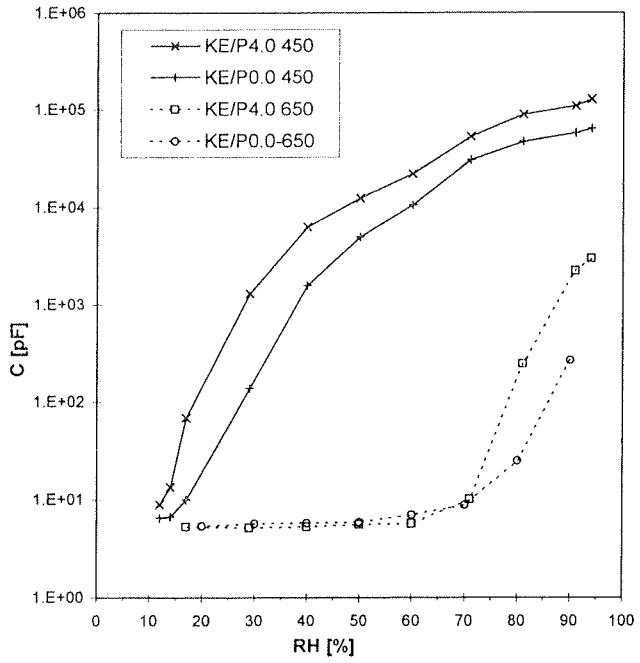

Fig. 5: The RH dependence of the capacitance of K doped thin films at 25°C. Sensors fired at 650°C for 1 h and at 450°C for 2 h. The frequency of the applied filed was 200 Hz.

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.

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