Electrical and structural characterisation of plasma-polymerized TEOS thin films as humidity sensors

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Abstract: In this study, we used plasma polymerization of TEOS to deposit thin water molecule sensitive layers on two intredigitated aluminum electrodes evaporated on glass substrate. Electrical and structural analyses of the deposited sensitive layers have been evaluated through current-impedance responses and FTIR spectroscopy. The elaborated humidity resistive sensor exhibited a detectable response to relative humidity (RH) percentages ranging from 20 to 95%. The films showed good sensitivity to water molecule due to the presence of hydroxyl groups OH. These groups provide the adsorption sites for water and play an important role to the humidity sensor properties. The low impedance, good sensitivity as characterized by a linear change in impedance from 10^6 to 10^3 Ω over RH interval of 20–80% and low observed hysteresis of about 4%, make the elaborated layer a promising candidate for humidity sensors development.

I. Introduction

Humidity control and monitoring have gained increasing concern in recent years, which greatly promoted the development of humidity sensors. It has become evident in the recent years that the influence of humidity is of paramount importance in diverse areas, such as moisture sensitive products, food processing, textile technology, storage areas, computer rooms, hospitals, museums, libraries, high voltage engineering and accelerator systems. In response to this situation, various kinds of humidity sensor (resistive-type and capacitive type) have been investigated and developed. The sensing materials are roughly classified into three groups: electrolytes [1, 2], organic polymers [3] and porous ceramics [4, 5]. Among various types of humidity sensors investigated, polymeric resistive-type sensors received much attention, due to their advantages of easy preparation, low price, high sensitivity, fast response and ready integration into integrated circuit. Organosilicon thin films elaborated in a glow discharge have received great interests as selective layers in chemical sensors development. These materials are advantageous because they usually have low fabrication costs, high thermal and chemical stability and adhere to various substrates. The use of plasma polymerized films as an insulating and coating for microelectronic devices are widely appreciated [6], however, they are not commonly used for the fabrication of absorbing layers. In order for film to be useful as sensitive layers, it must be homogenous, free of pinholes even at low film thickness, high thermal and chemical stability and good adhesion to various substrate materials. Films elaborated in a glow discharge can fulfil all these requirements. Plasma polymerization of organosilicon compounds has been shown to be able to absorb water vapour [7]. The ability of these layers to absorb water vapour and hence change its dielectric properties gave rise to investigate the humidity sensing characteristics of plasma polymerization of TEOS (pp-TEOS).

In this paper, low frequency plasma discharge (19 KHz) has been used to elaborate films from pure (Tetraethoxysilane) TEOS vapour. Electrical properties of the deposited sensitive films have been evaluated through humidity impedance characteristics, and its sensing properties have been investigated.

II. Experimental

II-1. Preparation of humidity sensor

The device concept consists of a resistive-type humidity sensor based on a thin polymerized TEOS films deposited on two-intredigitated aluminum electrodes. A sketch of the top view and the cross section of the sensor are depicted in Fig. 1.

The Al electrodes with spaces of 36 µm between tracks were evaporated on clean glass substrates. The advantage of sensors based on IDS structure is simple and cheap fabrication process and the ability to use sensor in a wide range of application without crucial changes to the sensor design.

Films were deposited using plasma enhanced chemical vapor deposition (PECVD) at low frequency (19 KHz)

in homemade and capacitively coupled parallel plate plasma reactor. The substrate was horizontally placed on the lower electrode and the reactor chamber was pumped down to 10^{-2} mbar. During deposition the discharge power and pressure were fixed to 10 Watts and 0.4 mbar respectively. Films thickness has been measured by a Tencor profile meter. Chemical structure of the elaborated layers has been studied

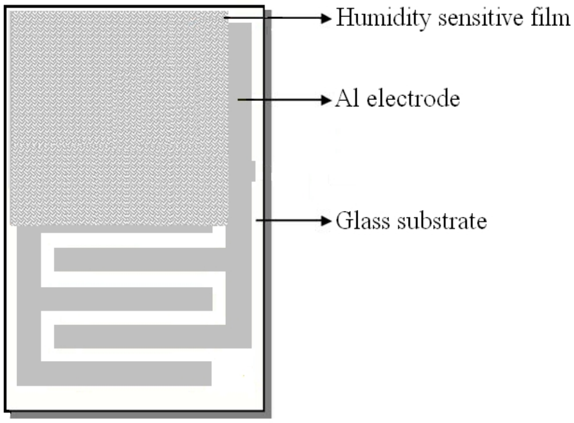

Fig. 1: Schematic top view of the sensor design

using Fourier Transform Infrared spectrometer (Nicolet Avatar 360 in the 400-4000 cm^{-1} range).

II-2. Sensor test

Response behaviours at different humidity level of plasma polymerization of tetraethoxysilane (pp-TEOS) based humidity sensor were evaluated in humidity chamber system.

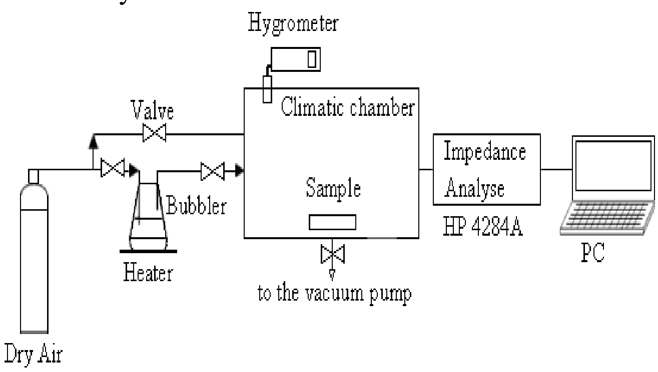

Fig. 2: Schematic view of the experimental set up

Shown in Fig. 2, Measurements have been performed in air with controlled humidity and temperature at atmospheric pressure. The humidity chamber volume is about 3526 cm^3.The relative humidity value is obtained by bubbling dry air in the humidifier containing distilled water that can be heated to 50 °C by means of a resistor. The relative humidity percentage inside the measurement chamber is controlled by two inlet valves. A temperature and humidity sensor (commercial Testo 610) was used to evaluate the relative humidity (RH) and to measure temperature stability in the testing cell. The evacuation of the chamber is performed by a mechanical pump. The electrical sensing properties were carried out by recording the impedance values of the sensors at different humidity level using HP impedance analyzer (4284 LCZ meter).

III. Results

III-1. Electrical sensing properties

The plasma polymerized TEOS thin films deposited on two-intredigitated aluminum electrodes were used as sensor element and evaluated for humidity detection under an applied voltage of 3V and signal frequency of 1kHz. Fig.3 shows the measured impedance responses over thin pp-TEOS film in the range of relative humidity (RH) of 10 - 95% at temperature of approximatively 25 °C. Over a wide range of RH from 20–95% RH, the sensor exhibits a sensitive response (impedance changes ~3 orders of magnitude) to humidity variation. Between 10 and 20 % of RH, the deposited films were found to be insensitive to water vapor. The pp-TEOS film sensor did not show a visible change of the electrical impedance, the value of this later was in order of about 10^6 Ω. Increasing RH beyond 20%, gives rise to an abrupt impedance decrease. The value of the electrical impedance decrease significantly until reaching the value of 10^3 Ω. At lower RH, the electrical response is caused by proton hopping between chemisorbed hydroxyl groups. Afterwards, when the amount of physisorbed water molecules starts to increase, the hydronyum ion, H_3O^+, is most likely the charge carrier. Furthermore, pp-TEOS-based sensor showed acceptable hysteresis of about 4% (Fig.3), which indicated that the reversible absorption/desorption is easily achieved in this case.

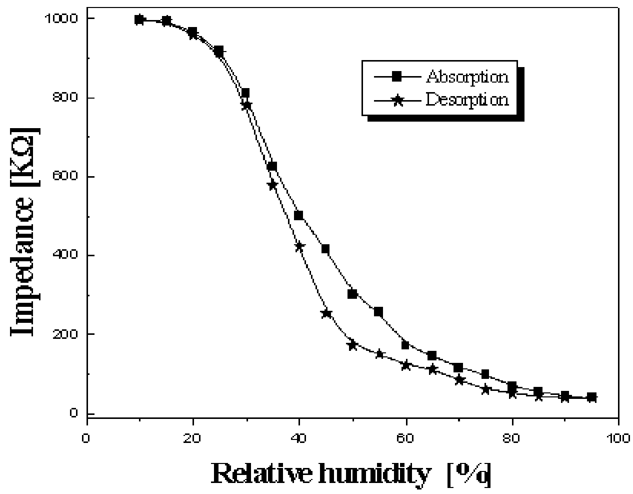

Fig. 3: Humidity hysteresis for pp-TEOS.

III-2. Structural properties

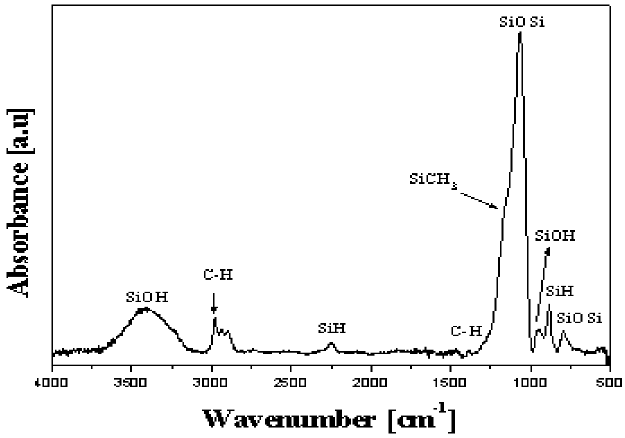

Fig. 4: Typical FTIR absorption spectrum of pp-TEOS film

To elucidate chemical structure and chemical composition of the deposited thin films, FTIR analyses were carried out in absorption mode. The resulting spectrum shown in Fig. 4 revealed several peaks assigned to chemical groups as it is listed in Table I. The spectrum of the plasma polymer deposited at 10 W from pure TEOS reveals strong peaks at around 800, 890 and 1062 cm-1, which, correspond respectively to Si-O-$(CH_3)_{1,2}$, Si-O-CH_3 and Si-O-Si groups. Another peak which is representative of the organic groups (Si-CH_3) appears at 1272 cm-1. The sensitivity to humidity is highly affected by the presence of the organic groups (Si-CH_3). The sensor properties can be improved by improving the wettability of the sensitive layer by incorporating oxygen, which can increase the polar oxygen species and reduce the methyl groups. However, FTIR spectrum shows also a peak with low intensity at around 3000-3700 cm^{-1} attributed to the stretching mode of surface silanol (Si-OH), which can contrary provides hydrophilic capability for water absorption through a hydrogen-bonding force.

TABLE I
ABSORPTION PEAKS RANGE AND THEIR ASSIGNMENTS

100% TEOS Wavernumner [cm^{-1}]	Group [8]
450	Si-O-Si
800	Si-O-$(CH_3)_{1,2}$
890	Si-O-CH_3
941	Si-OH
971	C-H
1062	Si-O-Si
1272	Si-CH_3
1410	C-H
1710	C=O
2242	Si-H
2967	C-H
3000-3700	Si-OH

III-3. Effect of pp-TEOS film thickness on the electrical sensing properties

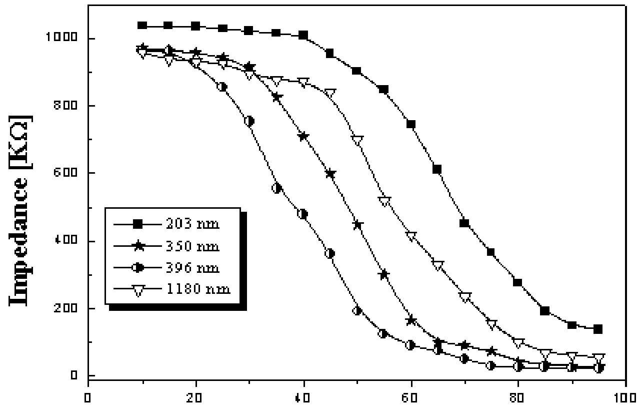

Fig. 5: Typical impedance response to humidity of pp-TEOS-based sensor with different thickness

Since the interpretation of the electrical response is based on the diffusion process of water in the vapour phase inside the sensing layer pores, the effect of the deposited film thickness on the electrical sensing properties has been investigated. During the plasma deposition process, both the discharge power and the monomer partial pressure were fixed to 10 W and 0.4 mbar respectively. Discharge time was varied in order to elaborate sensors with different layer thickness. The typical electrical response of humidity sensor based pp-TEOS is plotted in Fig. 5 for different film thickness.

Fig. 5 shows the impedance variation of the sensors in the whole humidity region (10 to 95% RH) for various film thicknesses. It is seen that all sensors have almost the same shape of response curve. However, incresing sensitive layer thickness beyond 693 nm decrease the sensor sensitivity. This behaviour may be attributed to film densification leading to the reduction in the size and also in the number of film pores.

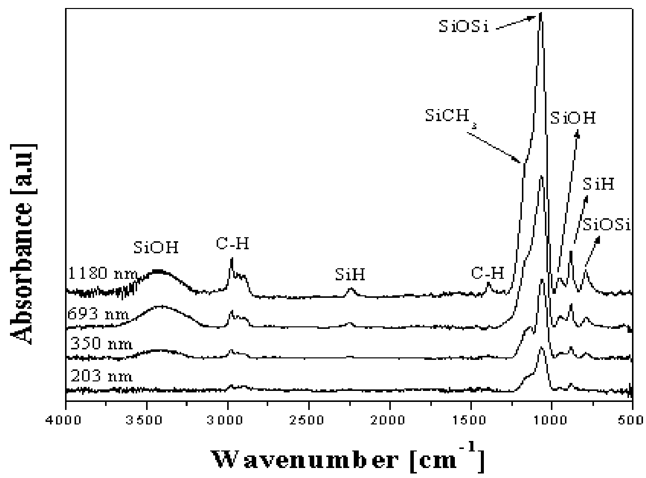

Fig. 6: FTIR spectra of thickness varied pp-TEOS

Rise of the film thickness, FTIR analyses were carried out in absorbance mode for four plasma polymerization process. The resulting spectra of the deposited layers achieved from pure TEOS at 10W are displayed in fig. 6. It is shown that intensities of $SiCH_3$ and Si-OH peaks at around 1272 cm^{-1} and 3660 cm^{-1} respectively, increases with increasing sensitive layer thickness. Fig. 6 also shows that as the thickness increases, the wave number corresponding to Si–O–Si stretching shifts from 1062 to 1063,5 cm^{-1} while the FWHM (full with at half maximum) decreases from 54,8 to 54,3 cm^{-1}. It has been reported [9] that an increase of the Si–O stretching wave number and a decrease of the FWHM which explains an increase in the film density.

IV. Conclusion

pp-TEOS films exhibit good electrical response to relative humidity for the investigated range of 10-95% RH with low hysteresis of about 4%. Electrical characterization showed that the sensitivity of the deposited layers to humidity was significantly decreased by increasing film thickness. This result was confirmed by Si–O–Si stretching absorption wave number and its corresponding FWHM. The presented preliminary electrical characterization results showed the viability of using plasma polymerization of TEOS for humidity sensors development but more detailed electrical characterization need to be carefully done in the future work.

V. Acknowledgment

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VI. References

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