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Humidity sensing properties of vacuum deposited thin polyimide layers

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The aim of this investigation is to study the humidity sensing properties of thin polyimide layers at room temperature. The layers are prepared by two different techniques – simultaneous deposition of the precursors on planetary rotating substrates and evaporation on linearly moving substrates (layer-by-layer). The influence of the layer thickness on the sensitivity to water vapour is also followed. As a measure of the sensitivity, the change in the electrical resistance as a function of the relative humidity in air is used. The resistance changes linearly in its semi-logarithmic graph, spanning over 4 decades. For studying the sensor response kinetics, the relative humidity is changed in a steplike manner, and the electrical resistance is monitored as a function of time. The fast response of the sensor could be related to dominant physical adsorption. The recovery process requires more time because it is not forced by heating or air flow through the vessel.

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1. Introduction

Humidity sensors have gained increasing applications in industrial processing and environmental control, and have been the subject of intensive study over recent years. Sensors of different types (based on changes in the dimensions of the sensing material, resistive, capacitive or cantilever sensors) use a polyimide (PI) thin film for water adsorption and desorption [1-3].

There are many reasons for selecting polyimide as the sensing material. It exhibits excellent thermal stability, a low dielectric constant and low equilibrium moisture content. It is resistant to irradiation, mechanically strong and chemically stable in the presence of most common contaminants. Also, polyimide processing is fully compatible with standard electronic processing procedures, an important consideration for cost control.

Thin vacuum deposited polyimide layers show a uniform and easy to control thickness, a lower dielectric constant compared to layers prepared by spin coating, and do not contain a solvent [4,5]. Their structure and electrical properties strongly depend on the preparation [1]. Preliminary investigations on polyimide layers obtained by vacuum co-deposition of the precursors 4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA) from independent sources, and subsequent thermal treatment, have shown that the structure and dielectric constant depend on the method used to form the layer. Layers grown continuously on planetary rotating substrates have a uniform bulk morphology, whereas in those built up layer-by-layer on linearly moving substrates, sublayers are clearly seen [6]; the latter have a greater dielectric constant [7]. After thermal treatments the surface of both layer types does not differ [6].

The aim of this investigation is to study the properties of thin polyimide layers prepared by both evaporation techniques as resistive humidity sensors working at room temperature. The effect of the layer thickness on the sensitivity to water vapour is also studied. Following the response kinetics, information about the sensing mechanism is obtained.

2. Experimental

The polyimide layer was formed on planetary rotating (30 rpm) or linearly moving (5 mm/s) glass substrates by vacuum co-deposition of ODA and PMDA (ratio 1:1) from two independent thermally heated Knudsen-type sources. The base pressure was $\leq 5 \times 10^{-4}$ Pa and the evaporation temperature 100 - 110°C for ODA and 120 - 145°C for PMDA. The deposition rate of the precursors, controlled by quartz oscillators, was 0.2-0.3 Å/s, and the thickness of the layers was 50 to 280 nm.

After deposition, the layers were thermally treated for 1 hour at 170 °C and subsequently 1 hour at 300 °C.

For electrical characterization of the layers, interdigitated Au electrodes were vacuum deposited through masks on top of the polyimide (electrode width 0.8 mm, distance between electrodes 1 mm). The samples were placed in holders having two Au pressure contacts. The sensor response to humidity, i.e. the change in the electrical resistance (R), was studied at 25°C by varying the relative humidity (RH) continuously or stepwise. The behaviour under gradually increasing or decreasing RH in the range 20-100% (R as a function of RH) was followed in a test chamber equipped with

temperature and RH controllers. For studying the sensor response kinetics under steplike changes in RH, the sensor was put alternatively in small closed vessels with saturated solutions of $(NH_4)_2SO_4$ and NaOH (maintaining constant RH values of 82 and 6% respectively) and the electrical resistance was monitored as a function of time. The measurement of R was performed with a multi-channel ohmmeter, using short electric pulses with alternate directions (± 10 V) thus keeping minimal polarization of the sample and precluding detrimental electrochemical migration. The control of the ohmmeter, the acquisition and processing of the data were computerized. The computer programs were created using LabView software.

3. Results and discussion

The variation of the sensor output (in Ohms) as a function of relative humidity (% RH) at 25°C, monitored under continuous rises or falls in RH, is shown in Fig. 1. The response curve reveals a close exponential relationship between the sensor resistance and RH, spanning over 4 decades of resistance when the relative environmental humidity varies in the range 10-95 % and is linearized by taking the logarithm of the resistance.

Fig. 2 presents the results obtained with the same sample under steplike changes in RH. The curve shows the sensor response kinetics for sharp drops or rises in relative humidity (6% and 82%). As can be seen, raising the relative humidity from 6 to 82 % causes a very fast change in R. The recovery process is slower, following an exponential dependence. Comparing Figs. 1 and 2, it is also seen that both methods of changing the relative humidity lead to equal resistance variations of more than 4 orders of magnitude.

It should be stressed that no influence of the preparation method and the layer thickness (50 or 280 nm) on the shape of the curves and on the values of R, measured at different RH, was observed.

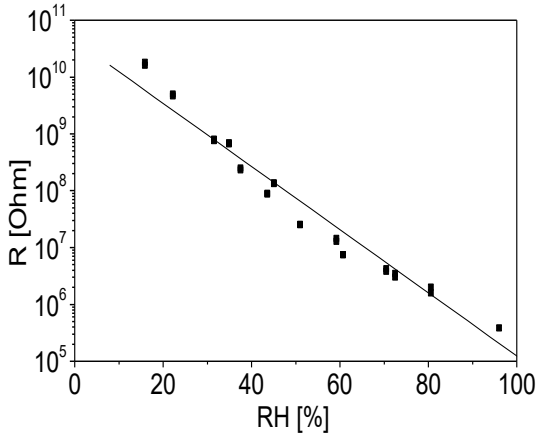

Fig. 1. Resistance change with relative humidity (RH) in a polyimide layer with d ≈ 50 nm, evaporated on planetary rotating substrates; thermally treated for 1 h at 170 °C + 1h at 300 °C; glass substrate, Au interdigital electrodes on top of the layer.

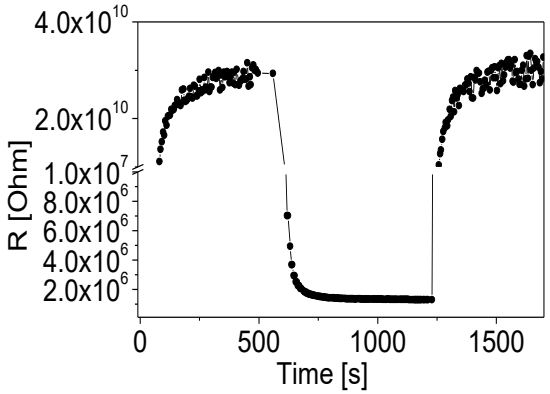

Fig. 2. Resistance change with time at 6 and 82% RH of the same polyimide layer as in Fig. 1.

The fast humidity response of the PI layers could be related to dominant physical adsorption, i.e. only the layer surface is involved in the sorption-desorption process. This explains the fact that it does not depend on the thickness of the layer, in the range of 50 to 280 nm.

Most likely for the same reason, the method used to grow the layer does not affect the behaviour of the thin PI as a humidity sensing material at room temperature. As mentioned above, after thermal treatment at 300 °C the surfaces of the layers have identical structures, regardless of the different bulk morphology (shown by SEM studies). Moreover, IR spectroscopy revealed that the annealed layers are fully imidized and do not differ in composition [8].

The recovery process requires more time because it is not forced by heating or air flow through the vessel.

4. Conclusions

The results presented in this paper show that thin layers prepared by vacuum co-deposition of ODA and PMDA from independent sources and subsequent thermal treatment reveal promising properties as resistive humidity sensors working at room temperature. They meet the requirements for high sensitivity, short response time and low power consumption. The sensing characteristics of the polyimide layers could be attributed mainly to physical adsorption. The preparation method is compatible with conventional microelectronic technology, and allows the development of smart sensors.

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