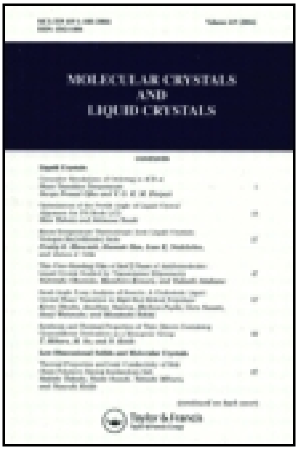
MOLECULAR CRYSTALS AND LIQUID CRYSTALS

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Improvement of Sensitivity and Response Speed of Capacitive Type Humidity Sensor Using Partially Fluorinated Polyimide Thin Film

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Version of record first published: 22 Sep 2010

Mol. Cryst. Liq. Cryst., Vol. 472, pp. 327/[717]–335/[725], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701548621

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We investigated the relationship between the relative humidity and the electrical capacitance of partially fluorinated polyimide thin films with the parameter of the thickness of polyimide, deposition angle of top Au electrode, and the fluorine content (in wt%) in polyimide. The electrical capacitance changed almost linearly over the humidity range of 0–80% RH. High sensitive polyimide humidity sensors were successfully prepared by adopting the double layered structure consisting of ultra thin anodic Ta_2O_5*(ca.50 nm) and polyimide (50 nm). The response speed of the sensors was also improved to less than 1s by oblique deposition of semi-transparent Au top electrode and the adsorption and desorption of water molecules proceeds more quickly by increasing the fluorine content of polyimide.*

Keywords: fluorinated polyimide; humidity sensor; oblique evaporation; response speed; tantalum oxide

INTRODUCTION

There has been a considerable interest in the low-cost practical humidity sensors having high sensitivity, accuracy, linearity, low hysteresis, long-term stability, fast response and negligible temperature drift. Especially, there is a strong need for reliable humidity sensors for low humidity condition and the techniques for detecting water molecules penetrating the film covering the sample has been getting

This work was supported by the CLUSTER of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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more important in the fields of meteorology, food factory, clinical, biotechnology, and manufacturing the electronic devices [1,2]. It is also known that the current degradation is faster when the organic devices are exposed to water vapor atmosphere Therefore, the demand for the ultra-high sensitivity of water molecules has been getting important [3,4].

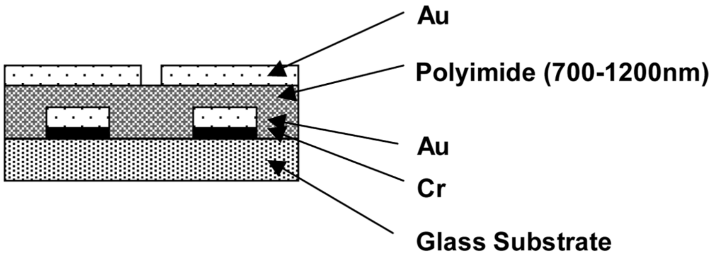
Many sensing techniques, such as capacitive measurement [5], resistive measurement [6], optic measurement [7], field effect transistors (FET) [8,9], surface acoustic wave (SAW) [10] and quartz crystal microbalance (QCM) [11,12] etc. have been developed to detect the humidity. Among them capacitive type and QCM seems to be a very stable and capable of measuring an extremely low humidity.

Polyimides are compatible with IC processes and have both chemical stability and long-term stability in a presence of moisture and heat, in addition to the good hygroscopic and dielectric properties. Therefore the capacitive type polyimide sensors have been extensively investigated. However, the typical polyimide humidity sensors suffered from slow response and substantial long-term drift and they were improved by introducing the cross-linked structure and fluorine atoms in the polyimide unit [13–16].

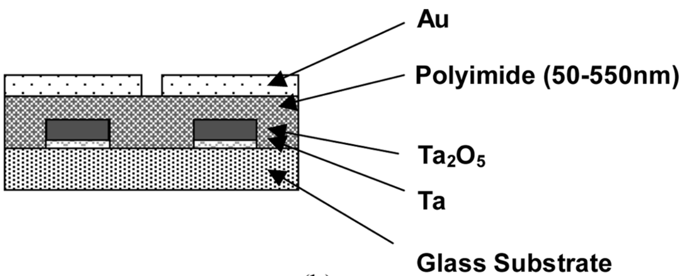
In this study, we investigated the sensitivity and response speed of capacitive type polyimide humidity sensors taking into account the film thickness, evaporation angle of Au top electrode, fluorine content of polyimide etc.

EXPERIMENTAL

We prepared two types of capacitive type humidity sensors, denoted as single layered device consisting of glass/Cr(10 nm)/Au (30 nm)/polyimide/Au structure and double layered device consisting of glass/Ta/Ta_2O_5/polyimide/Au structure as shown in Figure 1. The bottom electrode of single layered device was thermally evaporated, whereas, in double layered device, a 300 nm-thick Ta electrode was deposited by RF magnetron sputtering at room temperature from pure Ta target under Ar atmosphere. Anodization of Ta electrode was carried out in a 1 wt% citric acid solution at 30 V for 1 h. The resulting thickness of Ta_2O_5 layer was 50 nm. We used three types of polyimide with a different fluorine ratio of 0 wt%, 19 wt% and 31 wt%, which is denoted as KPI (Kapton type polyimide), FPI1 and FPI2, respectively. Polyamic acid, the precursor of polyimide, were dissolved in 1-methyl- 2- pyrrolidone (NMP) and spin-coated on Au or Ta_2O_5 layer. The polyamic acid films were pre-baked at 70°C for 15 min and then cured at 300°C for 2 h to obtain polyimide film. The resulting thickness of polyimide was



(a)



(b)

FIGURE 1 Configuration of single layered device consisting of glass/Cr(10 nm)/Au(30 nm)/polyimide/Au structure (a) and double layered device consisting of glass/Ta/Ta_2O_5 (50 nm)/polyimide/Au structure (b).

700 nm–1500 nm for single-layered device and 50–600 nm for double-layered device, respectively. After curing, the sample was soaked in ethanol for 3 min to remove the residual ions. Finally, Au top electrode was obliquely evaporated at the angles of 0, 30, 45 and 60°. The thickness of Au top electrode was 10 nm and the effective electrode area of the capacitor type humidity sensor was 25 mm^2.

The sensors were fixed in a stainless steel box (box1) which is placed in a constant temperature and humidity oven (box2, ESPEC SH241). The capacitance of humidity sensor was measured at the relative humidities (% RH) between 30–80% RH with 10% RH step at 30°C. Dry condition (0% RH) was obtained by closing the lid of box1 quickly and introducing the clean dry air at a flow rate of ca. 2 L/min, whereas the humid condition was obtained by opening the lid of box1 after stopping the dry air. Here, the cubic capacity of box1 and box2 was 0.18 L and 24 L, respectively. The frequency dependence of the electrical capacitance was measured by a LCR meter (Agilent 4284 A) at the frequency range between 100 Hz to 200 kHz. The response time of the humidity sensor was measured from dry condition (0% RH) to

80% RH and from 80% RH to 0% RH, respectively. Here, the electrical capacitance at 10 kHz was monitored at $\sim$10 samples per second by the computer connected to the LCR meter.

RESULTS AND DISCUSSIONS

Figure 2 shows the frequency dependence of capacitance and dielectric loss tangent tan δ in Au/FPI1 (1200 nm)/Au single layered device without ethanol treatment (ET) and in Au/FPI1 (1100 nm)/Au single layered device with ET measured at 0, 40 and 80% RH. The capacitance

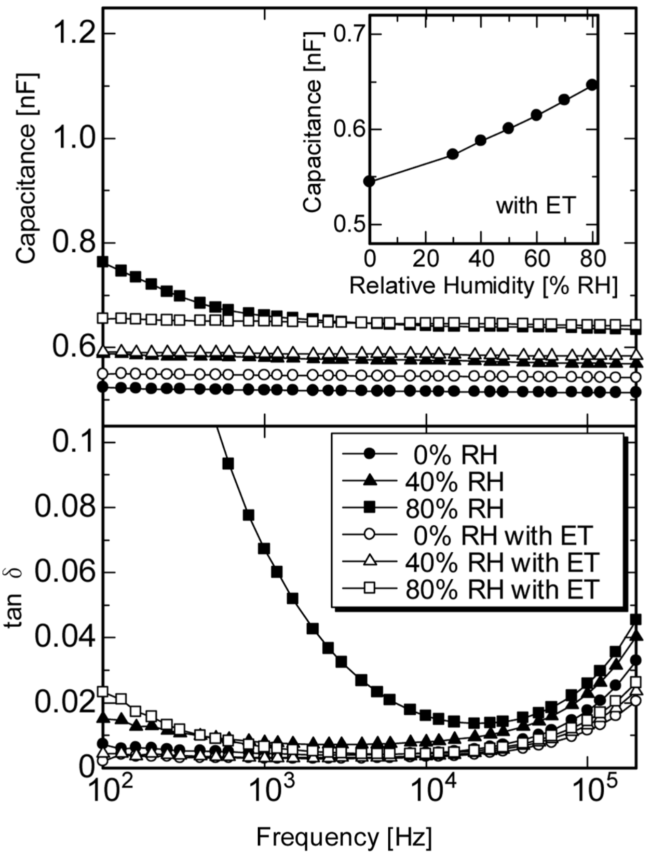


FIGURE 2 The frequency dependence of capacitance and tan δ in Au/FPI1/Au single layered device measured at 0, 40 and 80% RH with and without ethanol treatment (ET). Inset: The relationship between the capacitance and relative humidity in the device with ET.

of FPI1 film with ET is almost constant at the frequency range between 100 Hz and 100 kHz and the capacitance increases with the increment of relative humidity. On the other hand, the capacitance of FPI1 film without ET exhibits the large frequency dependence of capacitance and tan δ at low frequency in humid condition. This large tan δ observed at low frequency in humid condition is probably ascribed to the impurity ions in polyimide and most of impurity ion was successfully removed by ET. It should be noted here that the increment of tan δ above 100 kHz is not due to the physical properties of polyimide film but due to the time constant of the measured circuit defined as the product of the series resistance of electrode material and the capacitance of the sensor. The inset in Figure 2 shows the relationship between the capacitance and the relative humidity in Au/FPI1 (1100 nm)/Au device with ET measured at 10 kHz where tan δ becomes minimum. The capacitance of FPI1 film increases almost linearly with the relative humidity and shows negligible small temperature dependence at the temperature range between 30°C and 70°C (not shown here). The excellent linearity in the entire range of relative humidity and small temperature dependence of capacitance in partially fluorinated polyimide thin is faborable for humidity sensor application.

Figure 3 shows the transient response of the capacitance change, normalized as $(C(t) - C_0) \times 100/C_0$ (%), in Au/FPI1 (ca. 700 nm)/Au single layered device as a parameter of the angle of Au evaporation. Here, the thickness of Au top electrode is kept at 10 nm and C(t) is the measured capacitance at t second after opening the lid of box1 and C_0 is the capacitance measured at dry condition. The capacitance changes quickly within a few seconds and then reaches a constant value in less than 10 s, and the response speed increases with the increment of the angle. The normalized capacitance change at $t = 10$ s corresponds to the capacitance change between 0% RH and 80% RH in Figure 2. The very fast response in the device with obliquely evaporated Au is probably due to the creation of bypass for the water vapor in Au. Since it takes about a few second for the convection of humid air into box1, the intrinsic response speed of the sensor seems to be less than 1s judging from the slope in Figure 3. We therefore employed the evaporation angle of 45° for the devices discussed below.

Figure 4 shows the relationship between the capacitance and the relative humidity in Ta/Ta_2O_5 (50 nm)/FPI1 ($\times$nm)/Au double layered device. It should be noted here that the yield of the sample preparation was less than 20% in single layered device with a thickness less than 400 nm. On the other hand, we could successfully reduce the film thickness to 50 nm with high yield in double layered structure. The capacitance increases linearly with the increment of relative humidity

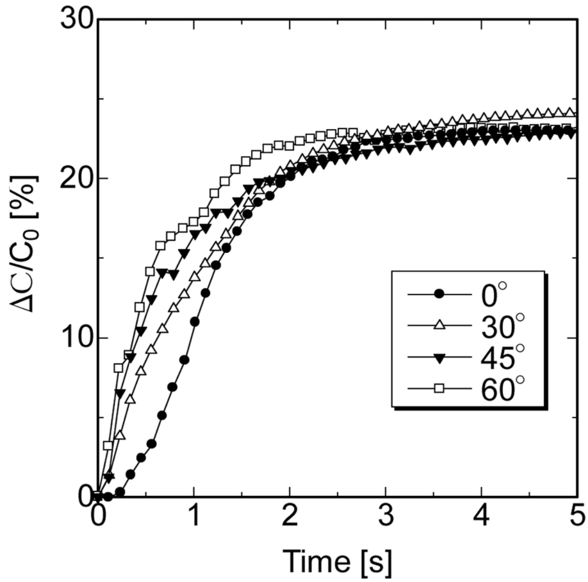


FIGURE 3 The transient response of the ratio of capacitance change in Au/FPI1/Au single layered device as a parameter of evaporation angle of Au top electrode.

for all samples. The inset in Figure 4 shows the relationship between the thickness of polyimide and the sensitivity of capacitive type humidity sensor defined as, $S(pF/\%RH) = (C_{80} - C_0)/(80 - 0)$.

Here, C_{80} and C_0 are the electrical capacitance obtained at 80% RH and 0% RH, respectively. Both the capacitance and sensitivity S changes almost inversely proportional to the thickness of FPI1 film, whereas the ratio of capacitance change $(C_{80} - C_0)/C_0$ is almost independent of the film thickness of FPI1. That is, the capacitance change is dominated by polyimide and the contribution of Ta_2O_5 for the capacitance change is negligibly small. As seen in Figure 4, the sensitivity of the sensor is estimated as 3.8pF/% RH and 45pF/% RH for the 550 nm- and 50 nm-thick polyimide sensor. This result is much larger than the other polyimide sensor, 0.13 or 0.19pF/% RH by Matsuguch et al., though it is difficult to compare the value itself if the thickness and the electrode area are different [13–16]. We therefore concluded that we have succeeded in fabricating the high speed and very high sensitive humidity sensor using double layered structure consisting of Ta_2O_5 and very thin polyimide film.

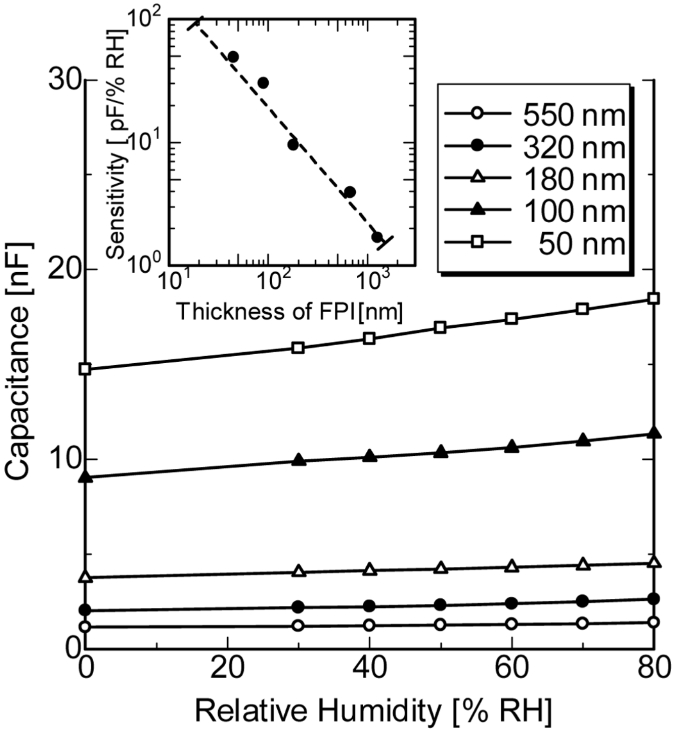


FIGURE 4 The relationship between the capacitance and the relative humidity in Ta/Ta_2O_5 (50 nm)/FPI1 (×nm)/Au double layered device. Inset: The relationship between the thickness of FPI1 and the sensitivity of capacitive type humidity sensor.

Figure 5 shows the transient response of the capacitance change in single layered KPI, FPI1 and FPI2 film from 0% RH to 80% RH and from 80% RH to 0% RH, respectively. Here, the thickness of each layer is about 700 nm. The capacitance of KPI in Figure 5(a) changes very slowly compared to partially fluorinated polyimide even though the normalized capacitance change at $t > 10$ s is larger than FPI1 and FPI2. In other words, faster response is successfully obtained by the increment of hydrophobic fluorine content in partially fluorinated polyimide film probably due to the moderate interaction with water molecules resulting to the fast adsorption and desorption of water molecules. The response of the capacitance in Figure 5(b) seems to be slower than Figure 5(a). Except for KPI case, it is not probably due to the slow desorption process of the adsorbed water but due to the experimental condition because it takes about 10 s to exchange

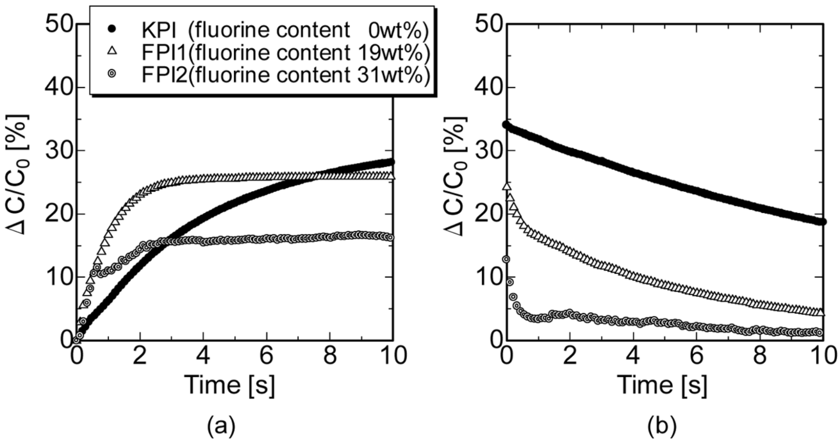


FIGURE 5 The transient response of the capacitance change in single layered KPI, FPI1 and FPI2 film from 0% RH to 80% RH (a) and from 80% RH to 0% RH (b).

the humid air by dry air in box1. The very fast capacitance change observed at first 1s in Figure 5(a) and (b) in FPI2 may be the intrinsic response speed of our humidity sensor.

CONCLUSIONS

In this study, we investigated the sensitivity and the response speed of capacitive type polyimide humidity sensors. Fast response speed of < 1 s was successfully obtained by the oblique evaporation of Au top electrode on partially fluorinated polyimide. The double layered structure contributes to the reduction of the thickness of polyimide film without short-circuiting the device. Both sensitivity and response speed were improved by decreasing the thickness of polyimide film in double layered structure and the very high sensitivity of 45 pF/% RH is obtained successfully. An excellent linear relationship between the measured electrical capacitance and the relative humidity in partially fluorinated polyimide film seems to be the favorable property for the humidity sensor though the ratio of capacitance change decreases with the fluorine content.

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