Abstract
In the present study, fast response resistive-type PI/multiwall carbon nanotube (MWNT) composite films were demonstrated. A composite film with a loading of 3 wt% MWNTs (PIC30) possesses a very linear response nature, a linearity correlation ($R^2$) of 0.99157 and a sensitivity of 0.00146%RH. The response time was less than five seconds and the resistance changed synchronously with different humidities. The recoverable and repeatable resistive responses affirmed the high efficiency of this film for fast humidity detection. A negative temperature effect was found and proper temperature compensation should be considered in the future applications. The surfaces of the films were found as an organized structure with nano-size dimples, which is helpful for absorption of water molecules. The proposed sensing mechanisms are discussed and it related with tunnel effects, doping of MWNTs by water and a barrier effect between CNTs.

1. Introduction
The life time of electronic products largely depends on the reliability of their packaging. One of the key factors which reflect the quality of an electronic package is its capability of resisting vapor [1-3]. However, silicon dies or circuits normally are enclosed in an isolated space and how to monitor the whole package in real time is a big issue. With the decrease of the sizes of devices, a higher degree of integration, and the diversity of microsystems, the in-situ measurement of humidity inside a miniature microelectronic package is crucial to monitor the healthy condition of a device [4]. Most commercially used humidity sensors with porous ceramics or metal oxides obviously are not suitable due to a large thickness or a complex integration process. In addition, the greater popularity of flexible electronics and microelectromechanical systems (MEMS) require compatible polymer sensors. Thus, the development of polymeric humidity sensitive materials which aims to predict the failure of microelectronic packages is imperative.

Polyimides (PIs), with high thermal stability and flexibility, are widely used as flexible substrates and dielectric interleavers in microelectronic packages. Extending the functions of PIs into a sensor is attractive, because it can be integrated directly in a package or even a semiconducting process as both a means of protection and sensors. There are normally two types of humidity sensors: capacitive-type and resistive-type. In fact, capacitive-type humidity sensitive PIs have been studied for a long time [5-7]. Capacitive-type sensors have the advantage of less power consumption, but the capacitance of a sensor relies on the frequency and is variable, which needs to be calibrated frequently. Resistive PI sensors were reported by Packirisamy et al. [8], which are much simpler and more straightforward than making capacitance measurements. However, the limitations such as non-linearly with humidity and a high cut-off relative humidity (42%RH) still cannot be ignored. For a real sensor, a wide range non-linear output signal requires more complicated and expensive signal processing circuitry for proper signal analysis and interpretation. Meanwhile, the high power consumption and appearance of a deviation in the measuring are serious drawbacks due to high resistance.

Carbon nanotubes (CNTs) are one of the most attractive nanoscale fillers because of their high aspect ratio, and combination of excellent thermal, electrical, and mechanical properties. Moreover, there are reports which have shown the response of CNTs to humidity [9, 10]. The vapor sensitive properties of polymer/CNT composites have been studied by many groups as well [11-13].

In this paper, fast response resistive-type PI/multiwall carbon nanotube (MWNT) composite films which are capable to monitor humidity inside microelectronic packages monitoring were demonstrated. The sensitivity, repeatable resistive response, temperature coefficient and the surface morphologies of PI/MWNT films were investigated. A PI/MWNT composite with 3 wt% of MWNTs showed a very linear response which can be used as a promising humidity sensor material with proper temperature compensation.

2. Experimental
Multwall CNTs (MWNTs, grown by chemical vapor deposition with a purity of 95%, a diameter of about 40-60 nm and a length of about 5 μm) were provided by ShenZhen Nano Tech. Pol, Co., Ltd (China). The surfactants - sodium dodecyl benzene sulphonate (SDBS, 90%, TianJin FuChen Chemical reagents Co., Ltd) and polyvinylpyrrolidone (PVP, PVP10-500G, Sigma-Aldrich) were used as received. The monomers - pyromelliticyl dianhydride (PMDA, 99%) and 4, 4-oxidianiline (ODA, 98.5%), and solvent N, N-dimethylacetamide (DMAC, 99.95%) were obtained from the International Lab. USA, and used without further purification.

The detailed experimental process of the synthesis of PI/MWNT composites by in-situ polymerization was reported in our previous paper [14]. In this paper, composite films with a loading of 3 wt% MWNTs (PIC30) were chosen to understand the sensing properties. Because the resistance of PIC30 film is lower enough for a resistive-type sensor. The films were peeled from the glass substrates and cut into strips with a size of 30×5 mm and a thickness of about 10 μm. Coplanar gold electrode patterns were sputtered on these films with a separation of 1 mm. The schematic view of setup of experiment is shown in Fig. 1. Before a sensing test, the films were thermally annealed in an oven at 85°C until the resistances were stable. Then the glass slide was put into an environmental chamber (PL-2FP, ESPEC) under desired
relative humidity (RH) and temperature. The resistances of the films were measured by a Keithley 617 source meter (using resistance measurement function) placed outside the chamber. The figures of resistances were read directly from the display on the meter. The surface morphologies of PI/MWNT composite films were studied using a scanning electron microscope (SEM Philips, XL40). All the studies focus on the down-side (stuck on the glass when curing) of the PIC30 film.

To understand the repeatability and response time of the PIC30 film, adsorption-desorption dynamic cycles between 30%RH and 90%RH were studied. Fig. 3(a) illustrates a time response and recovery curve of PIC30. Because the humidifier and dehumidifier of the chamber operated slowly, this dynamic test shows a response time of 8 minutes and a long time for recovery (10-16 minutes). Actually, the response of the film was very rapid. The fast response was shown in Fig. 3(b). The blue color spots is the resistance response of the PI/MWNT sensor, the black circle is the display by the sensor inside the chamber. The data were recorded every five seconds. It is found that our sensor gives fast response than the sensor inside the chamber. Although our data were collected every five seconds from the multimeter, the value changed obviously within five seconds. It is believed that the PI/MWNT sensor can detect the real-time change of humidity inside the chamber less than five seconds. The reference [16] reported the response time of MWNT networks, it is estimated that the response time is 3 seconds. The response time of our sensor is confirmed less than 5 seconds, which is comparable with a pure MWNT network.

3. Results and discussion

3.1 Sensitivity and fast response

From Fig.2, it can be found that the resistance of the PIC30 film increased with the increasing of RH, and a very linear response nature is observed from the linear fit results. The standard deviation ($R^2$) was 0.99157. The response of the PIC30 film at 50°C was also investigated and the linear behavior was still retained ($R^2$=0.99383).

The sensitivity ($S$) is defined by the equation as follows:

$$ S = \frac{\Delta R}{R_0} \cdot \frac{1}{\Delta(\%RH)} $$

where $\Delta R=R_{max}-R_0$, $R_0$ is the starting resistance of the film. Thus, the sensitivity of PIC30 is 0.00146%RH. The sensitivity of the PIC30 film is at a same level as reported in the reference [15], and less sensitive than the pure MWNT network (0.0056%RH) reported in the reference [16].
As we known, sorption and desorption of physical adorption of water due to van der Waals force is very quickly, which agrees with the repeatable and fast response results very well.

3.2 Temperature effect

The effect of temperature on the humidity sensing behavior of PIC30 is shown in Fig. 4. With an increase of temperature, the resistance of the film decreased, and this decrease is comparable with the change arising from the RH, so temperature compensation should be made when this film is used at different temperatures. This negative temperature effect indicates that the major conductive mechanism of PIC30 came from the inter-tube effect. A higher temperature provided more energy for the motion of electrons and decreased the barriers between MWNTs, which results in a decrease of the resistance of the film.

![Fig. 4 Resistance-temperature relationship of PIC30](image)

3.3 Microstructure of the surfaces of PIC30 film

The surface of the PIC30 film was observed by SEM and is shown in Fig. 5. A finer surface morphology with network-like dimple channels was seen on the down-side of the PIC30 film. The size of the dimples is less than 80 nm. It has not been confirmed that the size of the dimples is related with the loading of MWNTs, but a surface with smaller dimples possesses a higher specific surface area, which enhances the sensitivity of the film. It is thought that a surface with dimples is helpful for the absorption of water, so the PIC30 film can sense the environment more rapidly in only a few seconds.

![Fig. 5 SEM images of the surfaces of PIC30 film](image)

3.4 Proposed sensing mechanism

The increase of resistance of CNTs [17, 18] and polymer/CNT [12, 13, 15] composites due to moisture has been illustrated by former studies, but the mechanism of the increase of resistance is still under discussion. The issue can be analyzed in terms of two main effects. The first one is the increase of the intrinsic resistance of CNTs (R_c). The other reason is an increase of resistance between CNTs, the so-called inter-tubes effect (R_t and R_g). As is known, CNTs can be separated into metallic (M) and semiconductor (S) type according to their chirality, thus the resistance of a CNTs network largely results from the barrier of M/S types CNTs. Furthermore, because CNTs are surrounded by polymer molecules, the contact resistance of CNT-polymer-CNT needs to be considered. In this situation, hopping and tunnel effects play a crucial role for electron transfer. Fig. 6 gives a schematic view of the possible mechanisms; the resistance results from the tunnel effect (R_t) and the barrier (R_g) between MWNTs are changeable because of the separation of MWNTs. While, the doping effect by the water molecule induces a change of intrinsic resistance of MWNT (R_c). In our case of PIC30, an inter-tube mechanism (tunnel and barrier) is believable. The increase of resistance comes from the increase of the separation of MWNTs because of the swell of PI matrix.

![Fig. 6 Schematic view of the conductive mechanism in a PI/MWNT film](image)

4. Conclusions

In this study, the resistive humidity sensitivities of polyimide/multiwall carbon nanotube composite film was investigated. A film with a loading of 3 wt% MWNTs showed fast and linear response dependence with RH, which can be used as promising humidity sensors with proper temperature compensation. The change of resistance is at the same level of 10^4 ohm which is more effective and direct than a film with a
much larger change in the range of several exponentials, e.g. $10^4$-$10^{10}$. The proposed film demonstrates suitability to commercializing robust and economic polymer sensors. Moreover, this composite is suitable for monitoring microelectronic module packaging or integrating into a microfluidic system or biochip where information of humidity is required. There is the promise that the polyimide sensor developed is an excellent candidate for a miniature humidity sensor for long term precise electronic package monitoring.

Acknowledgments
We would like to acknowledge the financial support of the Strategic Research Grant (SRG) (Project No.: 7002443) in City University of Hong Kong for supporting this research and the financial sponsorship of PhD studentship from City University of Hong Kong for Mr. Qing-Yuan Tang.

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