Capacitive Moisture Sensor Devices
from Plasma Films

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Synopsis

Polymeric films were deposited on Al_2O_3 ceramic substrates by plasma deposition from trimethylsilyldimethylamine (TMSDMA) and bis(dimethylamino)methylvinylsilane (BDMAMVS), and their capacitance-relative humidity characteristics investigated. Films doped with methylbromide showed a linear dependence of log(capacitance) with relative humidity over the range 20–90% suggesting application on a moisture sensor device. Hysterisis effects were negligible and the response time was within 1 min.

INTRODUCTION

Many moisture sensor devices are commercially used to monitor the atmospheric environment in electronics technology, medical cares, and habitation. Most of these moisture sensors are composed of porous ceramics involving Fe_2O_3–K_2O, ZnO–Li_2O–V_2O_5, and $MgCr_2O_4$.[1] Humidity is determined from changes in electrical resistance or capacitance resulting from adsorption of water molecules on the ceramic surface. We reported that thin, plasma-polymerized polymeric films (1 μm thick) were available as moisture-sensitive materials for moisture sensor devices by which relative humidities of 20–90% RH could be detected by electrical resistance changes.[2] These plasma films having smooth surfaces, as moisture-sensitive materials, show significant advantages compared with porous ceramic surfaces. The water-adsorption process occurs rapidly, the response time is very short (< 20 s), and hysterisis in the resistance vs. humidity curve during cyclical humidity changes is negligible. If we obtain signal corresponding to humidity changes not as changes in electrical resistance but as electrical potential changes (capacitance changes), the potential changes can be amplified using MOS-FET (metal oxide semiconductor field effect transistor) to give more moisture-sensitive sensor devices.

A MOS-FET essentially consists of a source (acting as a donor of carriers), a drain (acceptor of the carriers), and to control the flow of carriers between the source and drain. If materials whose capacitance is moisture-sensitive are attached to the drain electrode, changes in humidity will alter the conductivity between the source and drain electrodes, resulting in amplified changes in the drain current as an output signal. Therefore, changes in capacitance at the drain electrode will result in amplified drain current changes.

This study represents a preliminary investigation into the preparation

of MOS-FET moisture sensor devices. The capacitance of thin plasma-polymerized films are investigated as a function of relative humidity.

EXPERIMENTAL

Plasma Polymerization. The apparatus used for plasma polymerization was reported previously.[3] The reaction chamber (35 mm inner diameter, 400 mm long) made of Pyrex glass is fitted with a monomer inlet, pressure gauge, vacuum system, and matching network for the inductive coupling of a 13.56 MHz frequency source. The experimental procedures were essentially the same as reported elsewhere.[2] The reaction system was evacuated to approximately 0.13 Pa using the combination of a diffusion and a rotary pump. The surface was exposed to an argon plasma for 10 min to eliminate water adsorbed on Al_2O_3 ceramic substrate surfaces. The system was again evacuated to 0.13 Pa, and monomer gas adjusted at a given flow rate and at a pressure of 1.3 Pa was injected into the reaction chamber. Plasma polymerization was initiated, and was continued at a level of 25 W rf power for 0.5–1 h.

Materials. Trimethylsilyldimethylamine (TMSDMA) and bis(dimethylaino)methylvinylsilane (BDMAMVS) as monomers were purchased from Petrach System Inc.

Quaternization. The plasma films deposited on Al_2O_3 ceramic plates were exposed in an autoclave to methylbromide vapor at 50°C and at 2×10^5 Pa for 48 h.[4]

Surface Energy. The contact angles for water, glycerol, formamide, diiodomethane, and tricresyl phosphate on plasma films deposited on a glass slide were measured by a drop-on-plate method using an Erma contact angle meter G-I with a goniometer. The contact angle data were analyzed to estimate the dispersive contribution γ_s^d, and polar contribution γ_s^p, according to Kaelble's method.[5]

Moisture Sensor Device. Three types of moisture sensor devices were prepared. Type I: Onto a ceramic plate (97% Al_2O_3, 8.2 mm diameter, 3 mm thick) (Kyocera Co., Ceramic 7R) an Au electrode (5 mm diameter) was deposited by vacuum evaporation, and then plasma films were deposited on the electrode. Finally the other Au electrode (3 mm diameter) was deposited by vacuum evaporation, thus sandwiching the plasma films between the orbicular Au electrodes. Type II: Plasma films were deposited onto the ceramic plate, and a pair of comb electrodes of Au attached by vacuum evaporation. Type III: The pair of comb electrodes of Au was evaporated first onto the ceramic plate, and then the plasma films were deposited over the comb electrodes. The comb of the types II and III is 3 mm long and 0.13 mm wide, with a separation of 0.19 mm between the two combs. The number of teeth in the comb is 7.5. These devices are schematically illustrated in Figs. 1(a) and 1(b).

The electrical capacitance of the devices was determined as a function of relative humidity using an Ando LCR Meter AG-4303 or a Hewlett Packard LCR Meter 4274 A. An Etac Humidity Chamber JLH-300 was used for controlling relative humidities of 20–90% RH at 40°C.

The film's thickness was determined by interferometry.
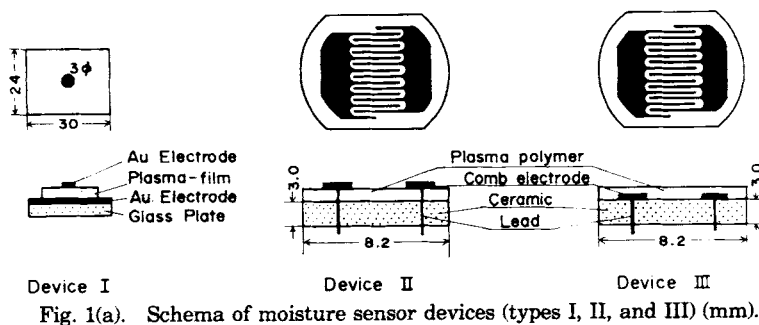
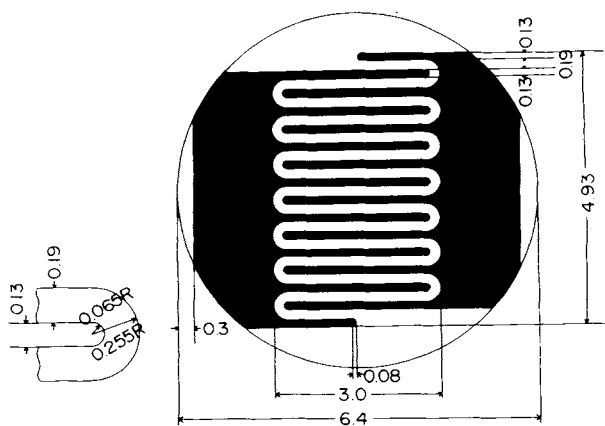Fig. 1(a). Schema of moisture sensor devices (types I, II, and III) (mm).

Fig. 1(b). Schema of comb electrodes (mm).

RESULTS AND DISCUSSION

Plasma polymerizations of TMSDMA and BDMAMVS yielded light-yellow, filmy polymers with elemental and chemical composition strongly influenced by polymerization conditions, especially the rf power and the monomer flow rate. These influences could be summarized by the W/FM parameter[6] which is a measure of the apparent input energy per mass of the monomer, where W, F, and M are the rf power (MJ/min), the flow rate of the monomer (mol/min), and the molecular weight of the monomer (kg/mol), respectively. The films were investigated by elemental analysis, infrared spectroscopy, and ESCA.[7] The plasma-deposited polymers are silicon polymers containing amide, amine, and amine–oxide groups. The hydrogen content decreases with increasing the W/FM value, while the nitrogen content increases. Preliminary experiments showed that moisture-sensitive plasma films require a balance between hydrophobic and hydrophilic groups,[8] and that the balance is favored in plasma polymerizations at relatively low W/FM values rather than at higher W/FM values.[7] Specimens used in this study, thus, were plasma films plasma-polymerized at a W/FM value of 143 MJ/kg for TMSDMA and at 103 MJ/kg for BDMAMVS. These two specimens could be distinguished on the surface by their surface energy. The surface energy was divided into two contributions, the disper-

sive (γ_s^d) and polar (γ_s^p) contribution, according to Kaelble's method.[5] The plasma films from TMSDMA possessed the higher surface energy of 28.5 dyne/cm (γ_s^d = 24.7, γ_s^p = 3.8 dyn/cm), but the polar contribution was low, plasma films from BDMAMVS possessed similar surface energy of 26.5 dyn/cm (γ_s^d = 16.6, γ_s^p = 9.9 dyn/cm) and the polar contribution was higher. This indicates that distribution of hydrophilic groups such as amide, amine, and amineoxide groups present in these plasma films may be different in the two films.

Frequency Dependence

The capacitance of the plasma film devices showed a strong frequency dependence of the electrical field applied between the electrodes. Figure 2 shows a typical capacitance–humidity plot for a type I device composing of a BDMAMVS plasma film as a function of frequency of the applied field. The higher the frequency of the electrical field, the smaller were the capacitance changes with changing relative humidity. This dependency may be due to a slow polarization rate of adsorbed water molecules,[9] and indicates that capacitance changes should be measured at low frequencies. In the following measurements all capacitance measurements were carried out at 120 Hz frequency, the lowest frequency on our LCR meter.
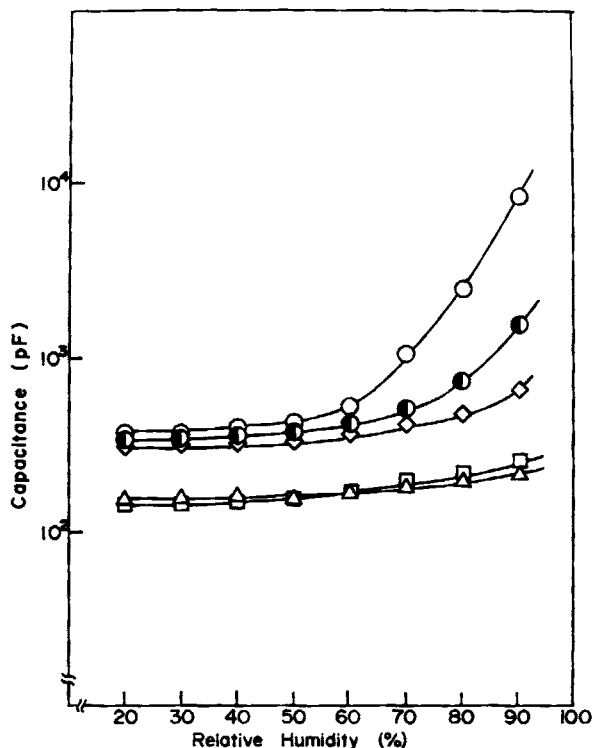

Fig. 2. Frequency dependence of capacitance (at 40°C) of plasma films (1.7 μm thick) from BDMAMVS; frequency: (○) 120 Hz; (●) 1 kHz; (◇) 10 kHz; (□) 200 kHz; (△) 2 MHz.

Influence of Electrode Construction

Three types of electrodes were examined for detection of capacitance changes at 120 Hz frequency with increasing relative humidity. The shape and structure of the three types of electrodes were described in the experimental part and schematically illustrated in Figure 1. The type I electrode, viz., a plasma film sandwiched between a pair of orbicular electrodes gave irreproducible measurements because of easy sparking across thin plasma films. The type II and III electrodes in which the Au comb electrodes were attached to the upper (type II) or bottom surface (type III) of the plasma films gave reproducible capacitance changes. Figure 3 shows the capacitance response for all electrode configuration as a function of relative humidity. The films, 1.7 μm thick, were deposited from BDMAMVS. The change in capacitance with relative humidity in devices I and II was low at low relative humidities (20–50% RH) but increased at higher humidities (> 50% RH). Similar changes in capacitance with varying humidity have been observed in the case of water adsorption on a silica gel surface, and has been attributed to mobile water molecules laying in multilayers on the first layer of immobile water bonded strongly with the surfaces.[9] With device III the logarithmic capacitance gradually increased linearly with relative humidity over the range 20–90% RH. This comparison indicates that the construction of device III may be better for detection of humidity than that of devices I and II.
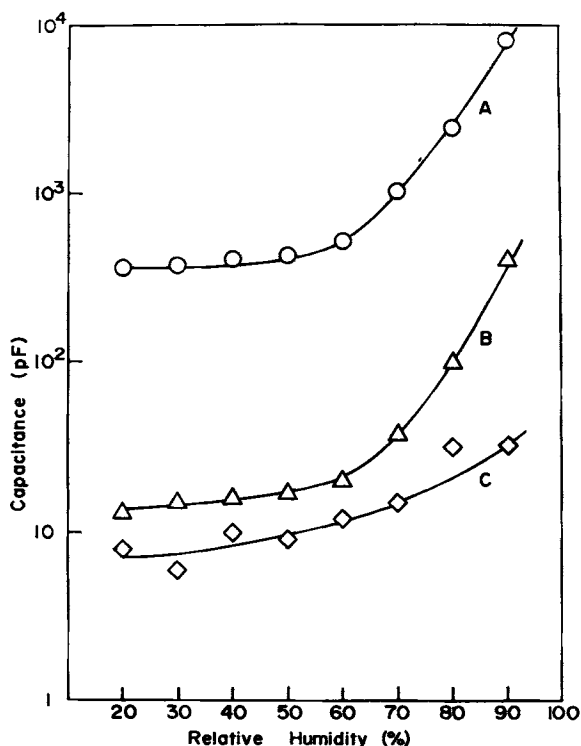

Fig. 3.   Electrode influence on capacitance (at 40°C and at 120 Hz) of plasma films (1.7 μm thick) from BDMAMVS: (A) device type I; (B) type II; (C) type III.

Effects of Quaternization

Changes in capacitance of the plasma films, as shown in Figure 3, could be used to detect relative humidities from 20 to 90% RH. To enhance sensitivity, the films were doped with methylbromide. This doping treatment has already been discussed in a previous paper[2] from the point of view of chemical composition changes using infrared spectroscopy and ESCA. Briefly, amine and amineoxide groups incorporated into films from TMSDMA and BDMAMVS during plasma deposition are partially quaternized by methylbromide vapor forming cationic groups of $-N^+H(CH_3)_2Br^-$ and $-N^+(CH_3)_3)Br^-$, and $-N^+(OCH_3)Br^-$, respectively.

Figures 4 and 5 show effects of the doping treatment on moisture sensitivity of the plasma films from TMSDMA and BDMAMVS. For the undoped plasma films from TMSDMA, as shown in Figure 4, the capacitance was 6 pF at 20% RH and 70 pF at 90% RH, while for the doped plasma
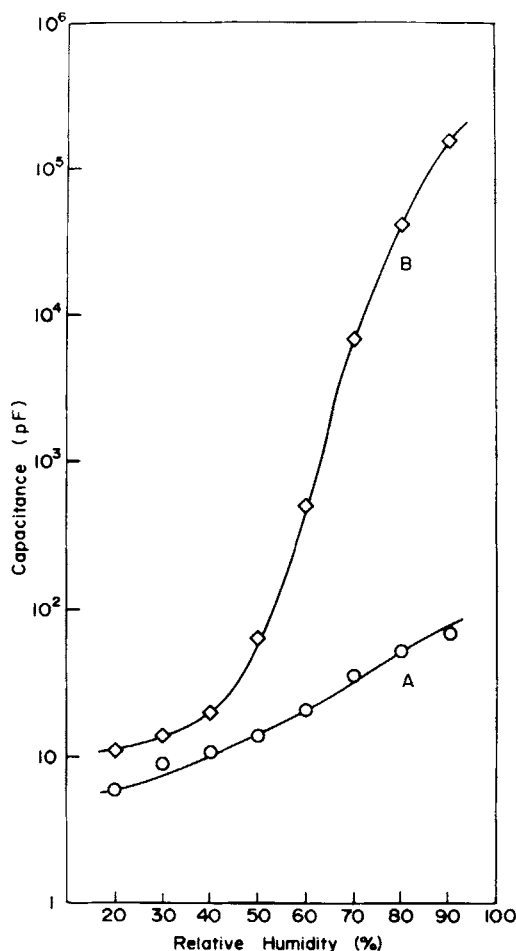

Fig. 4.   Capacitance (at 40°C and at 120 Hz) of undoped (A) and doped plasma films (B) (1.2 μm thick) from TMSDMA as a function of relative humidity.
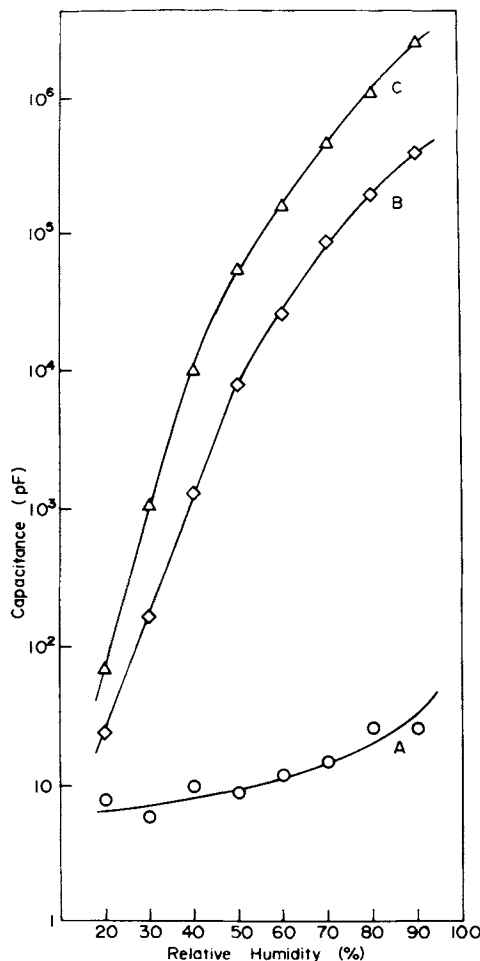
Fig. 5.   Capacitance (at 40°C and at 120 Hz) of undoped (A) and doped plasma films (B) (A, B, 1.4 μm thick, and C, 3.0 μm thick) from BDMAMVS as a function of relative humidity.

films the capacitance was 11 pF at 20% RH and 1.5×10^5 pF at 90% RH, i.e., an 11-fold increase for the undoped plasma films but a (1.4×10^4)-fold increase for the doped films. Similarly the plasma films from BDMAMVS showed capacitance changes enhanced by the doping treatment. The undoped plasma films from BDMAMVS showed a capacitance of 8 pF at 20% RH and 26 pF at 90% RH (3.3 times larger), while the doped films showed capacitance of 24 pF at 20% RH and 3.9×10^5 pF at 90% RH (1.6×10^4 times larger). These comparisons showed the marked improvement in moisture sensitivity resulting from doping with methylbromide. The doped films may even be applicable for practical moisture sensor devices without amplification using a MOS-FET.

The absolute capacitance of the doped plasma films, as shown in Figure 5, was thickness dependent, but the shape of the capacitance against relative humidity was similar. A typical hysterisis of the capacitance changes, when the relative humidity varied cyclically over the range of 20–90% RH, is shown in Figure 6 for the doped plasma films from BDMAMVS. The hys-
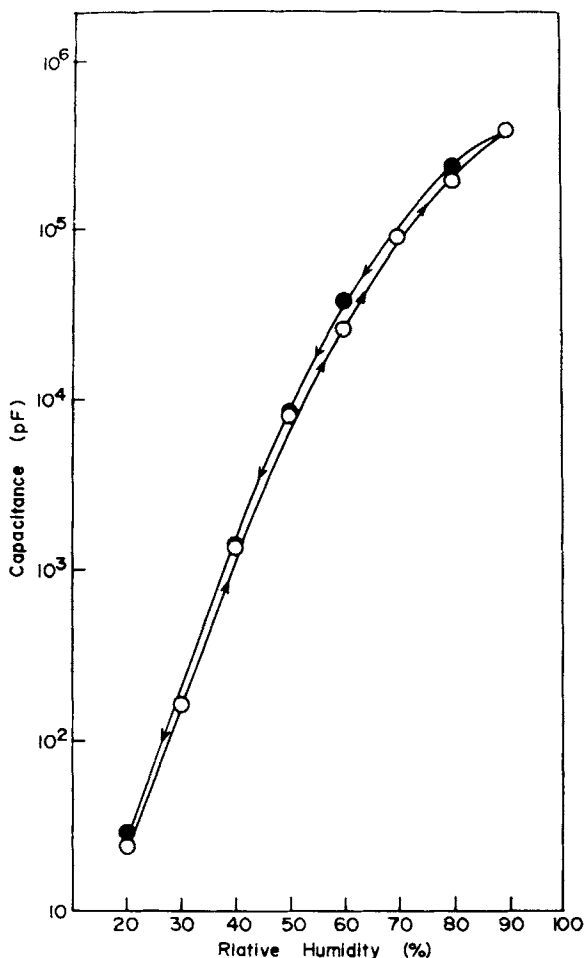
Fig. 6. Hysterisis of capacitance (at 40°C and at 120 Hz) of doped plasma films (1.4 μm thick) from BDMAMVS.

terisis was negligible and the response time was within 1 min, indicating rapid transport of water molecules through the plasma films.

In conclusion, this study demonstrates the application of plasma films to moisture sensor devices. The capacitance of plasma films polymerized from TMSDMA and BDMAMVS and then quarternized with methylbromide are moisture-sensitive over the relative humidity range of 20–90%. The logarithm of the capacitance increases almost linearly with increasing relative humidity over this range. Hysterisis was negligible, and the response time was fast (within 1 min).

References

1. T. Seiya, J. Shiokawa, S. Suzuki, and F. Fueki, *Chemical Sensors*, Kodansha Scientific, Tokyo, 1982.

2. N. Inagaki, *Thin Solid Films*, **118**, 225 (1984).

3. N. Inagaki, K. S. Chen, and K. Katsuura, *Kobunshi Ronbunshu*, **38**, 665 (1981).

4. N. Inagaki and A. Kishi, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 315 (1984).

5. D. H. Kaelble, *Physical Chemistry of Adhesion*, Wiley-Interscience, New York, 1971.

6. H. Yasuda, *J. Polym. Sci., Macromol. Rev.*, **16**, 1991 (1981).

7. N. Inagaki and K. Oh-ishi, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1445 (1985).

8. N. Inagaki, K. Suzuki, and K. Nejigaki, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 353 (1983).

9. S. Kurodaki, *J. Chem. Soc. Japan*, **73**, 606 (1953); *J. Phys. Chem.*, **58**, 320 (1954).