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Characterization of Al_2O_3 thin films prepared by spray pyrolysis method for humidity sensor

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Abstract

Al_2O_3 thin films were deposited on silicon, steel and nickel substrates to fabricate MOS and MIM devices. The films were prepared by spray pyrolysis method using a spray solution of Aluminium acetyl acetonate dissolved in dimethyl formamide and this solution was sprayed on to the hot substrates at temperatures of 300 and 350 °C. The films were amorphous in nature as detected by XRD. Capacitance versus voltage (*C*–*V*), current versus voltage (*I*–*V*) and capacitance versus frequency (*C*–*f*) measurements were taken for these films. MOS capacitor was used as a humidity sensor using the home made humidity sensor setup. ac capacitance and parallel resistance of the capacitor as a function of humidity were studied. It was found that the capacitance value increases from 0.537 to 2.073 nf with the increase in relative humidity (RH) from 0 to 90% and the resistance decreases from 153 to 93 kΩ with the increase in relative humidity from 20 to 87%. Relative dielectric constant versus temperature measurements were done for the MOS device to check its ferroelectric behavior and its critical temperature was found to be around 66 °C. MIM device was also used as a humidity sensor by measuring capacitance as a function of time by keeping the sensor in a dessicator. The 555 timer circuits were used to check the sensor behavior of the MOS device. Volume resistivity and breakdown electric field of the film deposited on steel were measured and found to be 5×10^{11} Ω cm and 5 MV/cm, respectively.

Keywords: Spray pyrolysis; Al_2O_3 thin films; Humidity sensor

1. Introduction

Al_2O_3 thin films are used in semiconductor devices as protective and insulating layers, as anti corrosive coatings [1] and as humidity sensors [2–4]. Al_2O_3–SiO_2 composite layers have great potential for memory application in microelectronics [5].

Various techniques have been used to deposit Al_2O_3 thin films, such as electron beam evaporation [6], spray pyrolysis [7], magnetron sputtering [8], MOCVD [9], off plane filtered arc method [10], etc. Spray pyrolysis has become one of the most widely used low cost and simple technique for the preparation of oxide films. Desired properties of the films can be obtained by varying the deposition parameters like substrate temperature, thickness, solution flow rate and molarity of the solution. Mansour et al. [6] have prepared Al_2O_3 thin films by electron beam evaporation with and without ion assisted deposition. They have reported that as deposited films were observed to be amorphous and annealing of these films at 800 °C in air for 12 h resulted in crystallization as seen in transmission electron micrographs (TEM).

Shamala et al. [11] studied the optical, electrical and structural properties of Al_2O_3 thin films prepared by spray pyrolysis and by electron beam evaporation. Optical parameters like absorption coefficient (α), extinction coefficient (k), optical band gap (E_g), and refractive index (n) were measured and found to be $2.2 \times 10^4\ cm^{-2}$, 0.006, 5.75 eV and 1.58 at 500 nm, respectively. Electrical parameters like dielectric constant (ε_r), electric breakdown field (E_B) was found to be 9.6 and 5.0 MV/cm, respectively. Aguiler-Frutis et al. [12] deposited Al_2O_3 thin films by spray pyrolysis and reported electrical characterization from *C*–*V* and *I*–*V* measurements of metal-oxide-semiconductor structure. They obtained a dielectric constant of 7.9 and breakdown electric field of 5 MV/cm. Nahar et al. [13] studied the humidity related properties of capacitive sensors employing

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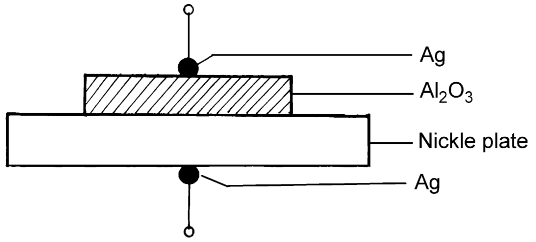

Fig. 1. Schematic diagram of the Al_2O_3 MIM device.

Al-porous Al_2O_3–Au structures prepared by anodization method. They observed that variation of capacitance is less at low RH and steeply rising at high RH for low current density films. However, the variation was reverse for high current density films.

In the present work, we have prepared Al_2O_3 thin films by spray pyrolysis method. MOS capacitor sensor has been fabricated by using Al_2O_3 thin films and studied the variation of capacitance as a function of relative humidity (RH) and temperature. Electrical parameters like dielectric constant and breakdown electric field were measured and optimized for the purpose of using Al_2O_3 film as a humidity sensor. A simple home made humidity setup has been developed in our laboratory and used it for humidity measurement.

2. Experimental

Al_2O_3 thin films were deposited on various substrates like silicon, steel and nickel at two different substrate temperatures of 300 and 350 °C by spraying a solution of Aluminium acetyl acetonate dissolved in dimethyl formamide.

Films deposited on silicon, nickel and steel were used to fabricate the devices like MOS and MIM to examine the films as humidity sensors and also to study their dielectric properties. Fabrication of MOS capacitor and its dielectric properties have been studied and reported by Shamala et al. [11]. Metal insulator metal (MIM) was fabricated in the following way. Al_2O_3 thin films were deposited on cleaned nickel plates of size 4 cm × 4 cm. On the surface of the Al_2O_3 film silver epoxy was made in the form of a dot of diameter 2 mm. On the bare side of the metal one more silver epoxy dot was made and two leads were taken from these two dots as contacts for making measurements. The schematic diagram of the device is given in Fig. 1. The thickness of the film was measured by gravimetric method and also verified by the reflection spectra taken for the films deposited on polished silicon substrate.

A home made dehumidifier is used to study the humidity response of the MIM and MOS devices.

Insulating properties of Al_2O_3 films prepared on steel substrates were studied using Impedance analyzer (Model HP4192A) and the volume resistivity of the films was measured using a high resistance meter (Model HP4339A).

The dielectric behavior of MOS with temperature was carried out using a home made furnace and a digital capacitance meter. The mild steel (MS 109 grade) substrates were cleaned by washing them with chromic acid, washed in running tap water and finally rinsed with distilled water.

3. Results and discussion

3.1. Capacitance versus RH percentage for MOS capacitor

Films deposited at 350 °C were used for the fabrication of MOS device and the device is used as a humidity sensor as these films have higher dielectric constant (9.60) compared to the films formed at 300 °C. Thickness of Al_2O_3 films is of the order of 130 nm. Variation of capacitance with percentage change in relative humidity (RH) was studied for Al_2O_3 MOS capacitor using a home made sensor set-up constructed with the help of existing literature [4] and it is shown in Fig. 2. Relative humidity measurement setup consists of air compressor, a set of helical tubes made up of copper, two air tight glass jars, sensor holder, capacitance meter and hygrometer to measure the RH.

By allowing the hot air through the tubes, we achieved almost zero RH and then by bubbling the compressed air through water the RH value was increased to 95% and corresponding increase in the capacitance was noted down. It was found that the capacitance increases slowly at low RH values (0–20%) and rapid variation at medium RH (25–50%) and there after the capacitance value becomes almost constant up to 90% RH as shown in Fig. 3. The temperature of the sensor in the humidity chamber was maintained at (27 ± 2 °C) for all measurements.

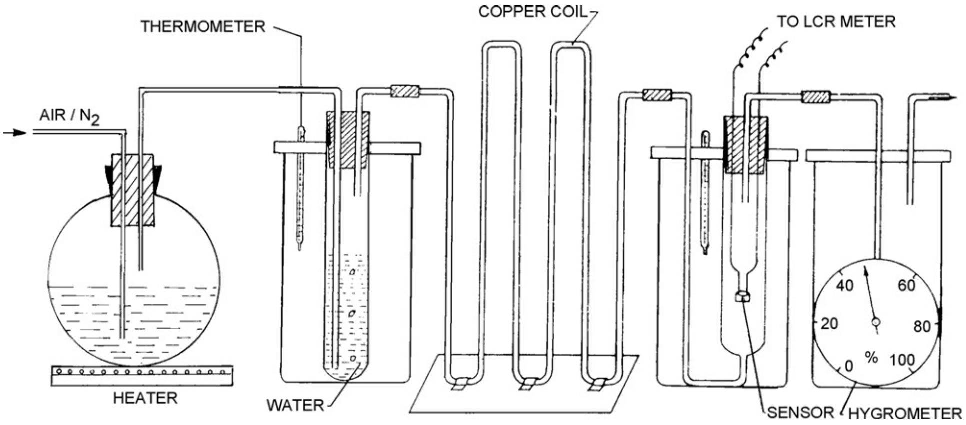

Fig. 2. Schematic of home made humidity measurement setup.

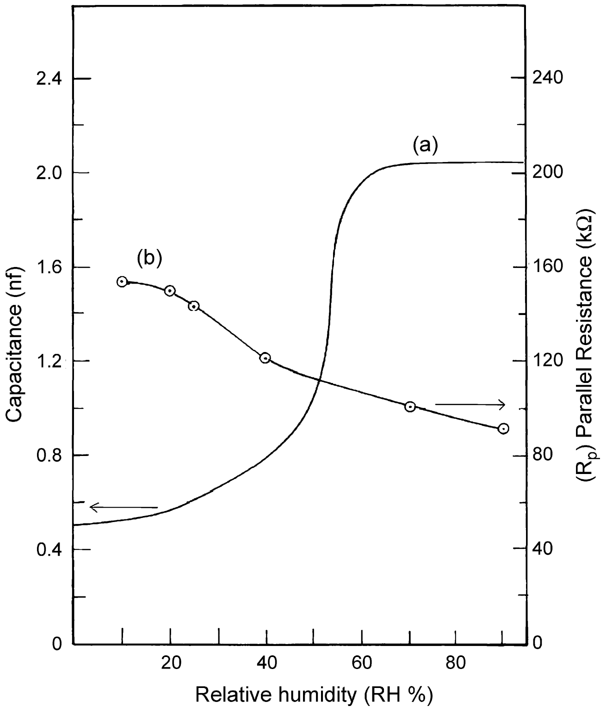

Fig. 3. (a) Capacitance vs. relative humidity (RH) plot for MOS device and (b) parallel resistance (R_p) vs. relative humidity (RH) for the same film.

However, Nahar et al. [14] measured the sensor characteristics at low humidity by sealing the sensor in glass tubes containing sulphuric acid solutions of known humidities. The variation of capacitance with low and medium (0–50%) RH values as observed by us is exactly similar to that found by them except the saturation part at high relative humidity found in our case. The increase of capacitance with RH (0–50%) is due to the absorption of water vapour in the film and it may due to the porous nature of the film. Variation becomes insignificant for higher RH values (above 50%), because the pores in the film are being filled completely with moisture and the sensor becomes insensitive.

3.2. Parallel resistance versus relative humidity (RH)

The resistance versus RH (relative humidity) variation was done for the same device using a mega ohmmeter and the plot is as shown in Fig. 3. It is found from the plot that the resistance of the device decreases with increasing humidity. The decrease in resistance with relative humidity is mainly due to the increase of water content in the pores of the film. For any porous dielectric film, it's surface conductivity (σ_w) increases with increase in the amount of water in the pores of the film. Once the pores are filled with water, the dielectric property will be dominated by electronic conductivity not by the ionic conductivity [4]. Hence the resistance decreases with increase in RH. Khanna et al. [4] have studied the effect of moisture on the dielectric properties of porous alumina films and reported the variation of both capacitance and resistance of MOS capacitor with the relative humidity. Variation of resistance with relative humidity, reported by us is similar to what they have observed. They have discussed this behavior on the basis of effect of moisture content in the pores of a dielectric material. They have also observed that the resistance decreased with increase of relative humidity.

This sensing behavior of the film can be explained by Sillers generalized mathematical theory [15]. Al_2O_3 thin film being porous, the moisture gets absorbed in the pores and contributes to the increase of dielectric constant, which varies with moisture content in the atmosphere as explained by the theory below.

The variation of real part of complex permittivity of Al_2O_3 with humidity is given by

$$\frac{d\varepsilon}{dh} = \left(\frac{d\varepsilon}{dq}\right)\left(\frac{dq}{dh}\right)$$

where $d\varepsilon/dh$ gives the variation of dielectric constant with humidity.

The first term on RHS gives variation of ε with volume fraction of adsorbed water (q) and second factor gives the variation of adsorbed water with humidity.

The volume fraction of water adsorbed (q) on the sensor at a given humidity is given by

$$q = \alpha\varepsilon_r V$$

where α is the film porosity, V the volume of water adsorbed by the film and ε_r is the relative permittivity of the film.

Due to gradual filling up of the pores, the permittivity of the film also increases which will result in the corresponding increase in the capacitance. It should be noted that the surface conductivity (σ_w) also varies with the amount of water layer adsorbed.

3.3. Variation of capacitance and relative permittivity with temperature

Al_2O_3 thin film capacitor (MOS) exhibits the properties of a simple capacitor. It is known that all ferroelectric materials are dielectrics but only few dielectrics show ferroelectric properties. One of the properties of ferroelectrics is that it has a critical temperature (T_c) below which it behaves like a ferroelectric and above which it is not. Critical temperature for a given material can be determined by plotting capacitance or dielectric constant versus temperature graphs. Hence capacitance/dielectric constant versus temperature measurements were carried out for MOS capacitor to check it's ferroelectric property. The sensor was kept at a constant humidity of 70% RH in a sealed enclosure and the temperature was varied from 50 to 150 °C. Variation of capacitance and dielectric constant with temperature is shown in Fig. 4. It was found from the figure that the capacitance is almost same up to 62 °C (0.054 nf) and then it increases slightly to 0.058 nf at a temperature of 66 °C. Further increase in temperature to 68 °C, the capacitance value falls to 0.055 nf, showing a small peak at 66 °C. With further increase in temperature, there is a sharp increase in the capacitance.

This behaviour can be explained on the basis of amount of moisture content adsorbed on the walls of the pores, conductivity of pores, etc. Nahar [3] has reported the effect of temperature on the capacitance of Al_2O_3 sensor and found that the capacitance variation is small up to 50 and at 55 °C, they have observed

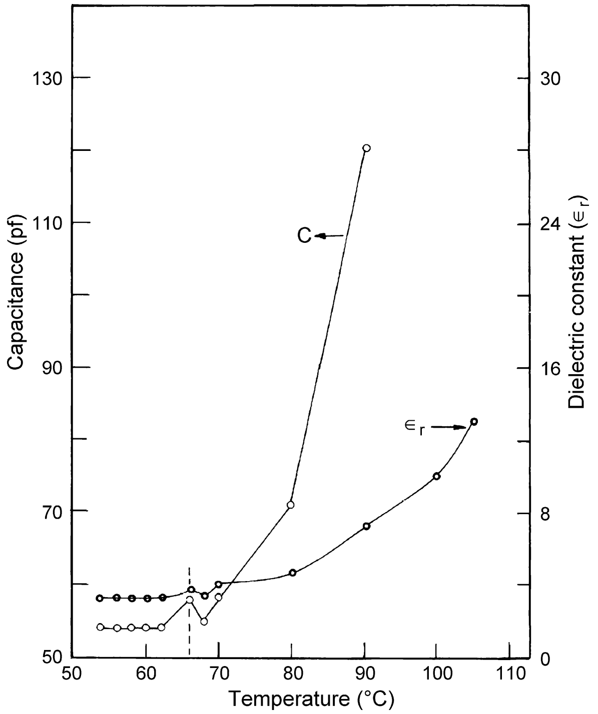

Fig. 4. Variation of capacitance and relative permittivity of the MOS device with temperature.

a peak in capacitance. They have explained this behaviour in terms of the amount of water adsorbed on the pore wall, the pore conductivity and the temperature of the sensor.

Variation of dielectric constant with temperature can also be explained on the same basis, as the capacitance and dielectric constant are of same nature. Ferroelectric properties of some of the dielectric materials were studied and reported [16].

3.4. 555 timer circuit

Humidity related properties can also be checked by connecting the MOS device to the timer circuit [17]. RH is the measure of the amount of moisture in ambient air as a percentage of the total amount of moisture that the air could hold at a given temperature. Ideal value of humidity is 35–65% indoors. Hence to measure the RH%, one can utilize a simple timer circuit to convert frequency to voltage output. The capacitance is indirectly recorded in terms of the out put voltage from the circuit. Experiments were carried out by connecting the MOS device and two leads were taken out from the device to measure the dc voltage. Increase in voltage shows the increase in capacitance with the moisture variation. Readings were taken at different weather conditions like a very hot and dry day (38 °C and 45% RH), moderate temperature day (28 °C), drizzling days and heavily raining days. It was found that the voltage was low (1.373 V) at dry and hot days, 1.49 V at moderate atmosphere, 1.59 V on rainy days and around 1.61 V on heavy rainy days. ac voltage was also measured simultaneously and it was found that the variation in ac voltage is opposite to that of dc voltage. The observations were shown in Table 1. The data presented in Table 1 was taken over a period of many months.

Table 1
The 555 timer circuit values for MOS capacitor

Weather	dc output (V)	ac out put (V)
Dry	1.478	1.1366
Raining	1.713	1.1345
Heavily raining	1.9040	1.0497

On the basis of theoretical treatment of dielectric thin films, some of the dielectric parameters like Fermi potential (Φ_F), work function for metal oxide interface (Φm), work function at the semiconducting-oxide interface (Φs), terminal voltage (V_T), intrinsic capacitance (C_i) and surface static charge Q_{ss} were calculated for the Al_2O_3 MOS device using standard methods [18] and the values are recorded in Table 2.

Formulae used are

(1) Fermi potential $(\Phi_F) = 0.0259 \ln(N_a/N_i) = 0.0259 \ln(10^{15}/10^{10})$, where N_a is the concentration of the acceptors and N_i is the intrinsic concentration.
(2) Depletion width $W_m = 2(\varepsilon_0 \varepsilon_r \Phi_F / qN_a)^{1/2}$, ε_r is the dielectric constant of the Al_2O_3 film (9.6), ε_0 is the permittivity of free space (8.85×10^{-14} F/cm^2), and q is the electronic charge.
(3) Work function at the semiconductor-oxide interface $\Phi s = 2\Phi_F$.
(4) Charge per unit area in the depletion region $Q_d = -qN_a W_m$.
(5) $V_T = -Q_d/C_i + 2\Phi_F$.
(6) Capacitance per unit area in the depletion region $C_i = \varepsilon_0 \varepsilon_r A/d$, where ε_0 is the permittivity of the free space and ε_r is the relative dielectric constant of the film, A is the gate area of the MOS capacitor (2.893×10^{-3}) cm^2 and d is the film thickness.
(7) Interface trap charge Q_i can be calculated using the relation $V_T = \Phi_{MS} + 2\Phi_F - (Q_i + Q_d)/C_i$, where Φ_{MS} is the work function difference between the metal and the semiconductor.

These calculated values are in good agreement with the experimental values and also with the reported values of an ideal MOS capacitor of Al–SiO_2–Si system [18].

3.5. Humidity related studies on MIM capacitor

MIM capacitor of thickness 170 nm was used for the measurement of capacitance variation with change in humidity. For this

Table 2
Dielectric parameters for an ideal Al_2O_3 MOS capacitor calculated using theoretical treatment

Work function at semiconductor-oxide interface (Φ_s)	0.596 V
Charge per unit area in the depletion region (Q_d)	1.232×10^{-8} C/cm^2
Fermi potential (Φ_F)	0.298 V
Depletion width (W_m)	7.7×10^{-5} cm
Terminal voltage (V_T)	0.796 V
Intrinsic capacitance C_i	6.12×10^{-8} F/cm^2
Intrinsic charge (Q_i)	5.5×10^{-8} C/cm^2

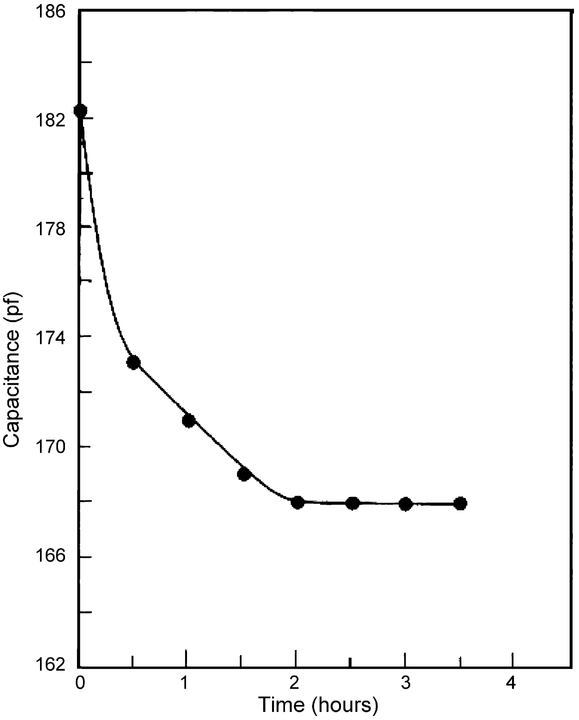

Fig. 5. Plot of capacitance vs. time for MIM device.

purpose home made setup containing a desiccator with absorbing gel, capacitance meter, and MIM device were used. Two contacts were taken from the device, one from the film surface and other from the back surface of nickel using silver epoxy. Capacitance was measured in the presence of air using the capacitance meter and it was found to be 0.17 nf. Immediately the device was put in the desiccator with an absorbing gel inside and tightly closed. It was observed that the capacitance value was increased from 0.174 to 0.182 nf. Then the value of capacitance decreases with time and after a long time, it attains saturation at 0.16 nf as shown in the Fig. 5.

The variation of capacitance for two different conditions mentioned above can be explained as follows. Al_2O_3 dielectric film, being a porous material and having humidity absorbing nature, when kept in the desiccator, the film absorbs the moisture from the gel which is already wet. As the capacitance is directly proportional to the dielectric constant which in turn depends on the amount of moisture present in the desiccator initially, the capacitance value increases. But it gradually decreases with time, which shows that even the gel being an absorber of moisture, starts absorbing the moisture from the film. This will continue till the equilibrium state is reached after a long time.

3.6. Al_2O_3 on steel

Films deposited on nickel substrates were also characterized for their dielectric properties by measuring their volume resistivity, breakdown electric field (E_B) and variation of capacitance and relative dielectric constant with frequency.

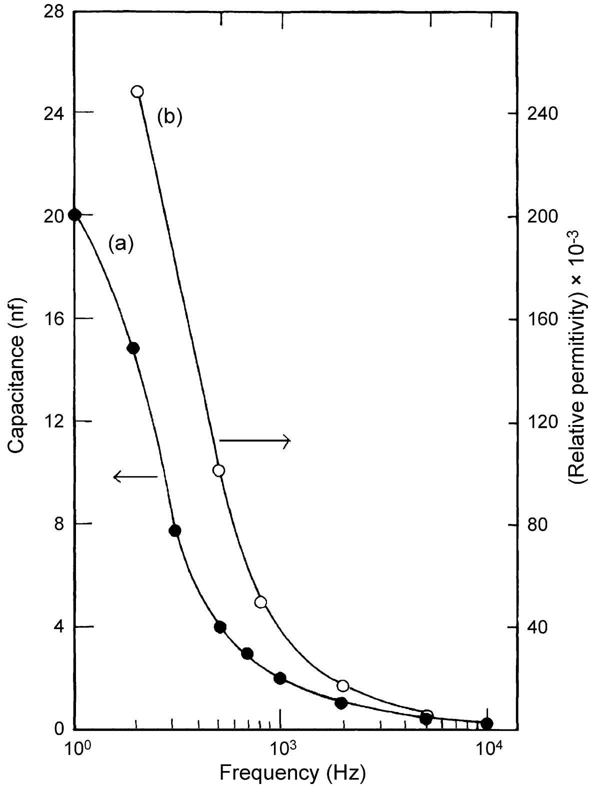

Fig. 6. (a) Capacitance vs. frequency for Al_2O_3 deposited on steel and (b) relative permittivity vs. frequency for Al_2O_3 deposited on steel.

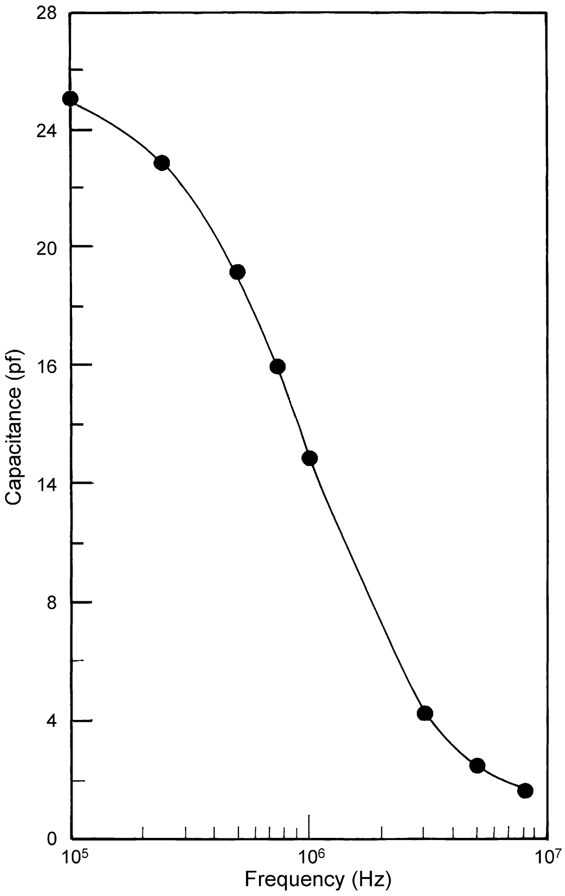

Fig. 7. Variation of capacitance with high frequency (100 kHz to 15 MHz).

Bulk resistance and volume resistivity of the film of thickness 150 nm were found to be 1.5 MΩ and 5×10^{11} Ω cm, respectively. The formula used for volume resistivity was *RA*/*d*, where *R* is the bulk resistance, *A* the contact area (5 cm^2) of the film with the meghometer lead and *d* is the film thickness. The same film was subjected to a very high voltage to check its dielectric strength and it was found that it can with stand a field up to 5 MV/cm which is same as that of the Al_2O_3 MOS device reported in our earlier paper [11].

Variation of capacitance and relative permittivity at low and high frequency (100 Hz to 10 KHz) for the same film was plotted in Fig. 6. It was seen from the figure that the capacitance decreases rapidly in the low frequency range and then shows slow fall and becomes almost constant (0.03 nf) beyond 40 K Hz.

The frequency response of the above film was studied by measuring the variation of capacitance with frequency in the range 100 kHz to 15 MHz. Plot of Frequency versus capacitance is shown in Fig. 7. It is found from the plot that the capacitance decreases rapidly from 25.35 to 2.46 pf with the increase in frequency from 100 kHz to 5 MHz and it becomes almost constant (1.8 pf) at higher frequencies. Beyond a frequency 15 M Hz, the variation in capacitance is negligible, as the film cannot respond to such high frequency.

4. Conclusions

Al_2O_3 thin films were prepared by spray pyrolysis method on different substrates like silicon, nickel and steel to study their dielectric properties in connection with humidity sensor. Devices like MOS and MIM were fabricated and tested as humidity sensors. Variation of capacitance is studied as a function of RH, frequency and temperature. MOS capacitor shows slow increase in capacitance at low humidities, rapid increase at medium RH and the capacitance is almost constant at high RH values. Ferroelectric behavior of the MOS device is also observed and it is found that it has a critical temperature of 66 °C. Volume resistivity of the film deposited on steel was found to be 5×10^{11} Ω cm and a breakdown electric field (E_B) of about 5 MV/cm which is a characteristic of good dielectric film. Variation of parallel resistance of the MOS device with relative humidity was also studied and observed that the parallel resistance of the device decreases with increase in humidity.

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