

Dielectric properties of $\text{Fe}(\text{OH})_3$ thin films formed at solution–gas interface

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Abstract. Dielectric properties of solution–gas interface-formed $\text{Fe}(\text{OH})_3$ thin-film capacitors ($\text{Al}/\text{Fe}(\text{OH})_3/\text{Al}$) of various thicknesses have been studied in the frequency range $10\text{--}10^6$ Hz at various temperatures (300–443 K). Dielectric constant, ϵ , increases with increasing film thickness (d) and temperature (T) and decreases with increase of frequency (f). The loss factor ($\tan \delta$), showing pronounced minimum with frequency, increases with rise of temperature, and $\tan \delta_{\min}$ shifts to a higher frequency. The large increase in dielectric constant towards low frequency region indicates the possibility of an interfacial polarization mechanism in this region.

Keywords. Capacitance; dielectric constant; loss factor; interfacial polarization; microscopic field distortion.

1. Introduction

Compound thin films are of great importance due to their semiconducting and insulating properties. These films can be prepared by many techniques. Chemical deposition is one among them. However, nonavailability of the exact chemical reaction restricts this type of film deposition to a large extent. It has been reported that thin films of Ag_2S , PbS (Nikam and Pathan 1994a, b; Nikam and Shinde 1994) and $\text{Fe}(\text{OH})_3$ (Nikam and Pathan 1994c) can be prepared by initiating a chemical reaction at a liquid–gas interface. In the present study, a similar method was used to prepare ferric hydroxide thin films by a chemical reaction involving ferrous sulphate solution and ammonia gas. The electrical properties of $\text{Fe}(\text{OH})_3$ films prepared by using chemical deposition method were recently reported by Nikam and Pathan (1994c). The following is the only report of dielectric properties of $\text{Fe}(\text{OH})_3$ films formed at the interface of aqueous ferrous sulphate solution and ammonia gas.

2. Experimental

The experimental set-up used for preparing $\text{Fe}(\text{OH})_3$ films was similar to the one reported earlier (Nikam and Pathan 1994c). One hundred ml of 1% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (BDH AnalaR 99.78%) aqueous solution in a dish was exposed to NH_3 (BDH AnalaR 99.78%) gas for about 1–3 min. A thin uniform layer of ferrous hydroxide of a light green colour was formed at the surface of the ferrous sulphate solution. Ferrous hydroxide film thus formed was picked up on a clean glass substrate with vacuum-evaporated (thickness ~ 200 nm) aluminium base electrode. The glass substrate was dipped in distilled water to remove soluble impurities. It was taken out, dried and kept in a desiccator. The thickness of the film produced depended upon the exposure of ferrous sulphate solution to the ammonia atmosphere. Due to

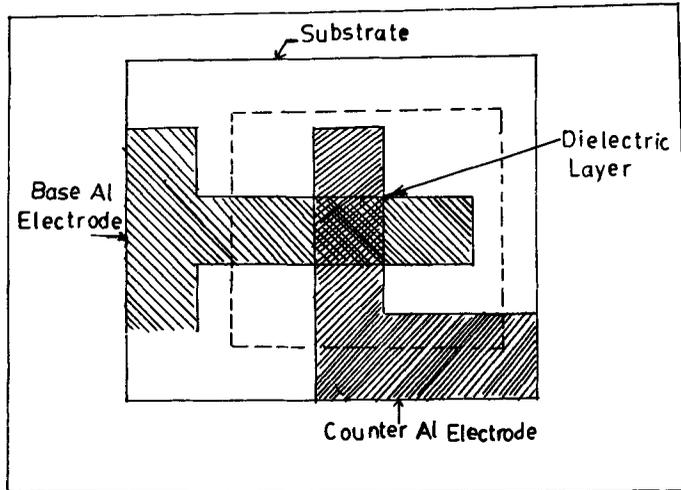


Figure 1. Electrode configuration of Al/Fe(OH)₃/Al capacitor.

precipitation on long exposure of ferrous sulphate solution to ammonia gas, the thickness of the film cannot be increased beyond certain limits. Thick films peeled off while thin films adhered well to the glass substrate. When the ferrous hydroxide film was taken out of the ammonia atmosphere, it absorbed oxygen with great avidity at room temperature and turned into yellowish brown ferric hydroxide. Pure aluminium was again vacuum-evaporated on the film to complete the Al/Fe(OH)₃/Al capacitor (figure 1).

The composition of the ferric hydroxide films was determined colorimetrically (Charlot 1964). This colorimetric analysis showed that the composition of the film was Fe_{1-x}(OH)₃, possibly due to the presence of Fe²⁺ in it; *X* varied from 0 to 0.2 for thick and thin films respectively. X-ray diffraction study of the Fe(OH)₃ films revealed amorphous structure.

Al/Fe(OH)₃/Al capacitors with effective area ranging between 0.6 and 1 cm² were stabilized by annealing them in vacuum of the order of 10⁻⁵ torr at ~140°C for 6 h. The film thickness was measured with a multiple beam interferometer (model-Michelson). Capacitance (*C*) and loss factor ($\tan \delta$) of MIM structures were measured at different temperatures (300–433 K) and frequencies (10–10⁶ Hz) for films of different thicknesses (*d*), using a digital Agronic bridge (model-57) provided with internal as well as external generators along with a null detection system in a vacuum of the order of 10⁻⁵ torr. The temperature was recorded by a chromel–alumel thermocouple. Values of loss factor ($\tan \delta$) were calculated from the relation

$$\tan \delta = \frac{\sigma}{\omega C}, \quad (1)$$

where ω is angular frequency given as

$$\omega = 2\pi f,$$

and σ the electric conductance of the capacitor.

3. Results and discussion

Figure 2 shows the variation of capacitance and dielectric constant with film thickness at room temperature. It is seen that dielectric constant increases with increase of thickness and attains a constant value of 1.1 at $d \sim 3400 \text{ \AA}$. The values of capacitance (C), dielectric constant (ϵ), thickness (d), area (A) of the film and free space permittivity (ϵ_0) are interrelated by the equation (Peek *et al* 1985)

$$C = \frac{\epsilon\epsilon_0 A}{d}. \quad (2)$$

Therefore (2) explains the variation of C and ϵ with d in the present studies. At lower thicknesses ($< 1500 \text{ \AA}$) the value of ϵ decreases rapidly. This can be attributed to a contribution to the capacitance from an aluminium native oxide thin layer of about 3–4 nm thickness that might be present on the lower aluminium electrode (Hino *et al* 1988). The increase of ϵ with increase of thickness of the film can be ascribed to the increase in grain size with increase in thickness of the film (Horikawa *et al* 1993). ϵ decreases with increase of f at all temperatures, but this variation is less pronounced as the temperature decreases. This is ascribed to an interfacial polarization caused by space charge and microscopic field distortion (Dutta and Barua 1983).

The most significant features of a.c. behaviour of $\text{Fe}(\text{OH})_3$ film capacitor are the loss minimum ($\tan \delta_{\min}$) in the frequency curve and its shift to higher values and to higher frequencies with increasing temperature and *vice versa* (figure 3). This is true for all film thicknesses. Assuming that Al/ $\text{Fe}(\text{OH})_3$ /Al junction shown in figure 1 is an electrical insulator with a conductance σ and capacitance C , $\tan \delta$ of the junction is theoretically calculated on the basis of the equivalent circuit illustrated in figure 4 and based on the model suggested by Kushida *et al* (1993). Accordingly $\tan \delta$ is given

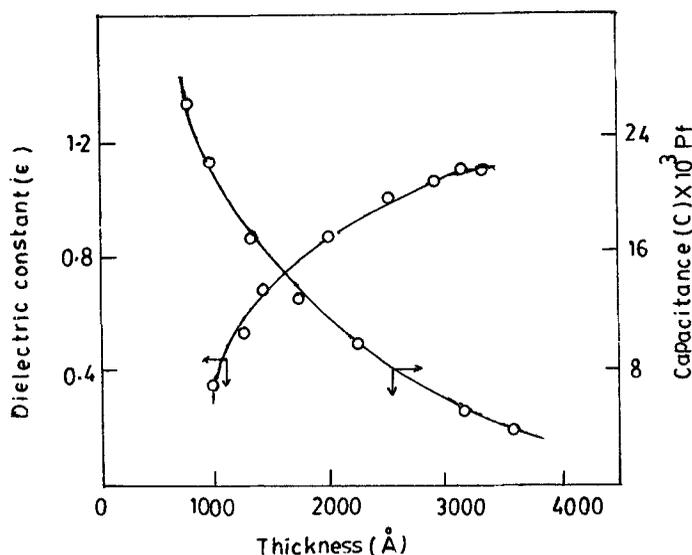


Figure 2. Capacitance and dielectric constant vs thickness of the film.

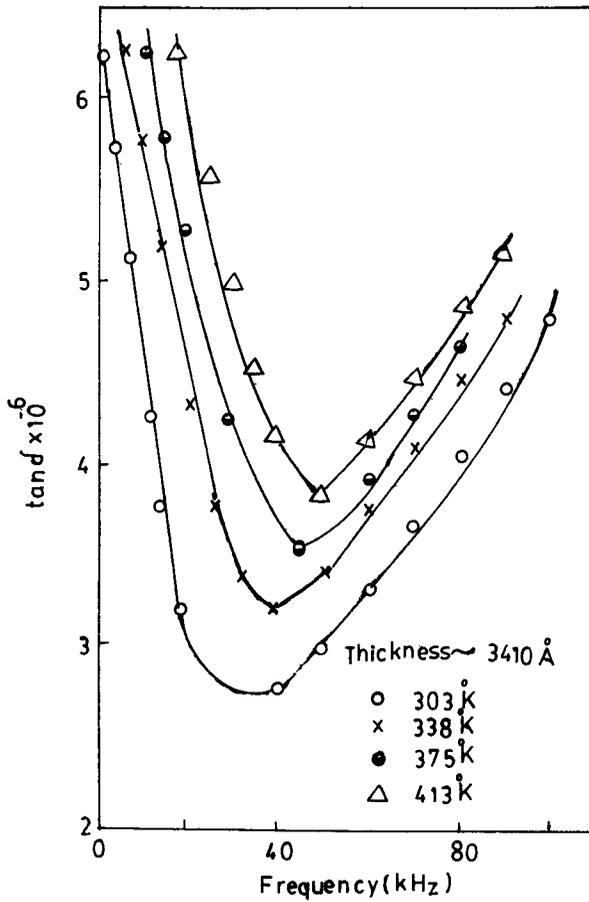


Figure 3. Tan δ vs frequency for a film of thickness $\sim 3410 \text{ \AA}$.

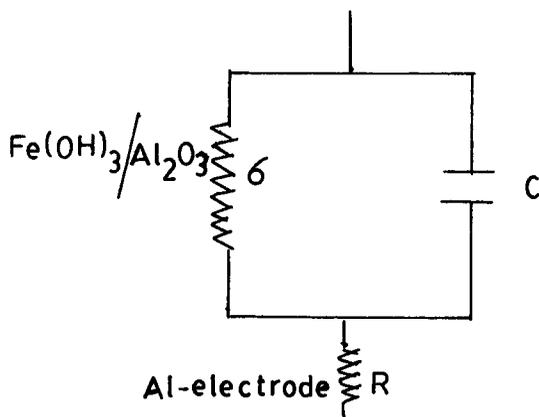


Figure 4. Equivalent circuit for Al/Al₂O₃/Fe(OH)₃/Al junctions.

by

$$\tan \delta = \frac{\sigma(1 + R\sigma)}{\omega C} + \omega R\sigma, \quad (3)$$

where R is the electrical resistance of native oxide layers formed on bottom Al electrode. From (3), the minimum of $\tan \delta$ appears at the frequency f_0 satisfying the relation

$$\omega_0^2 = (2\pi f_0)^2 = \frac{\sigma(1 + R\sigma)}{c^2 R}. \quad (4)$$

From (3), the slope of the $\log(\tan \delta)$ vs $\log(f)$ curve in the range $< \omega_0$ becomes approximately -1 and that in the range $> \omega_0$ becomes 1 . These characteristics are observed in the curves shown in figure 3.

Since σ will decrease considerably with lowering of temperature (Nikam and Pathan 1994 c), R remaining practically unchanged, ω_0 will also be lower at low temperature. Thus a shift of ω_0 would be to a lower frequency at low temperatures and *vice versa*. The values of ε and $\tan \delta$ increase with increase of temperature at all frequencies. The large increase of all these parameters beyond 343 K may be attributed to ionic motion in the form of dipolar orientation. Similar results have been reported earlier (Nikam and Pathan 1994c). Thus the grain size effect certainly influences the dielectric constant with increase of temperature can be related to an increase of grain size with temperature which in fact is observed from the thermal recycling studies of the films (Nikam and Pathan 1994 c). Thus the grain size effect certainly influences the dielectric constant and its temperature dependence in the $\text{Fe}(\text{OH})_3$ films. It may be pointed out that the dielectric conductivity ($\sim 10^{-6}$ mho/cm) is proportional to $\tan \delta$. Thus as the temperature increases, the conductivity of the $\text{Fe}(\text{OH})_3$ film and hence $\tan \delta$ would also increase.

Activation energy values obtained from plots of $\log \omega$ vs $1/T$ (not shown) for four constant capacitances (Nikam and Pathan 1994 b) were compared with those obtained from resistivity measurements (Nikam and Pathan 1994 c). These values differ slightly due to instrument errors ($\pm 0.5\%$).

Therefore it is concluded that $\text{Fe}(\text{OH})_3$ films formed by using solution-gas interface technique exhibit grain size effect on dielectric properties.

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