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Electric and dielectric properties of solution–gas interface grown amorphous AgCl films

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Abstract. Electric and dielectric properties of solution–gas interface grown AgCl thin film capacitors (Al/AgCl/Al) of various thicknesses have been studied in the frequency range 10^1–10^6 Hz at various temperatures (303–393 K). I–V characteristics show ohmic, space-charge-limited, and thermionic emission conduction mechanisms to operate at low, intermediate and high voltages respectively. Capacitance decreases with increasing film thickness and applied frequency while it increases with increase of temperature. Loss factor ($\tan\delta$), which shows a pronounced minimum with frequency, increases with the rise of temperature and $(\tan\delta)_{\min}$ shifts to a higher frequency. The large values of capacitance and dielectric constant (ε) in the low frequency region indicate the possibility of an interfacial polarization mechanism to operate in this region while electronic and ionic polarizations dominate in the high frequency region.

Keywords. I–V characteristics; space charge limited currents; thermionic emission; capacitance; dielectric constants; loss factor.

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1. Introduction

Thin films of AgCl find applications in electrochemistry [1], ion sensitive membrane [2], coated wire electrodes [3] and in ion sensitive field transistor [4]. However, AgCl films formed by conventional thermal evaporation, sputtering and electrodeposition are impure, defective and nonstoichiometric [5–9]. Therefore, we have used, for the first time, solution–gas interface technique to give chemically and mechanically stable films of AgCl. The previous investigations of thin films of AgCl formed by using different techniques are restricted only to structural, optical and electric conductance studies [6, 9–18]. This is the only investigative study of I–V characteristics and dielectric properties of AgCl films formed at the interface of aqueous solution of 0·5% $AgNO_3$ and HCl gas.

2. Experimental

One hundred ml of 0·5% $AgNO_3$ aqueous solution in a dish was exposed to HCl gas atmosphere. The AgCl film formed on the surface of the solution was picked up on an ultrasonically cleaned glass substrate with evaporated (~ 2000 Å) aluminium base electrode. The film was washed 2–3 times by dipping it in warm distilled water to remove impurities followed by drying under a vacuum of $\sim 10^{-2}$ torr. Pure aluminium was again evaporated on the film to complete Al/AgCl/Al capacitor

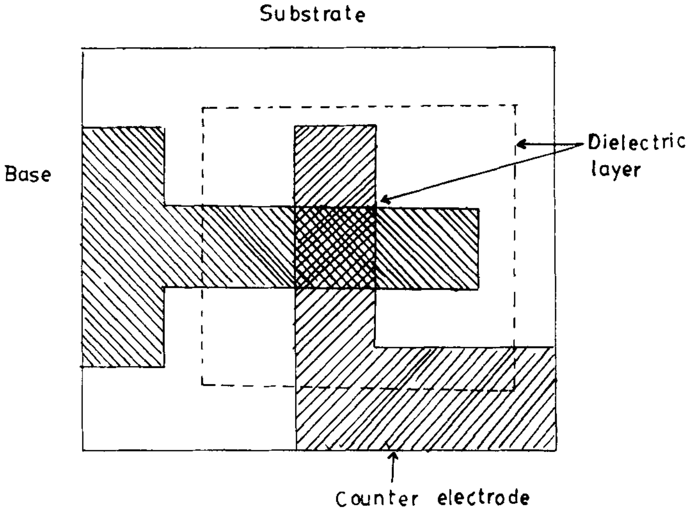

Figure 1. Configuration of Al/AgCl/Al capacitor.

(figure 1). All capacitors were of sandwich type. They were stabilized by keeping them at room temperature for several days in a vacuum desiccator, and later on annealing in vacuo of $\sim 10^{-5}$ torr at about 413 K for 6 h. Calorimetric analysis at 620 mμ wavelength [19] of AgCl films confirmed that films were more or less stoichiometric. The XRD study showed amorphous structure of the films. The dielectric thickness was measured with a multiple beam interferrometer with an accuracy of ±20 Å. Capacitance and loss factor were measured at different frequencies (10^1–10^6 Hz), at different temperatures (303–393 K) for films of different thicknesses (2000–4000 Å), using a digital Agronic bridge (model-57) provided with internal as well as external generators along with a null detection system in a vacuo of $\sim 10^{-5}$ torr. Films of lower thicknesses (< 2000 Å) were discontinuous and those of higher thicknesses (> 4000 Å) peeled off.

Methods employed to measure electric conductivity and I–V characteristics of these capacitors of different dielectric thicknesses at various temperatures were similar to those reported earlier [20, 21].

3. Results and discussion

Figure 2 shows the variation of $\log R$ versus $1/T$ curves for AgCl film of thickness $\sim 2000 \pm 20$ Å. AgCl films exhibit semiconducting behaviour. Energy of activation (ΔE) values obtained from these curves (figure 2) are listed in table 1. Figure 3 shows typical I–V characteristics on a log–log scale. It is seen from these characteristics that, at low voltages I–V curves are ohmic ($I \propto V^1$), over intermediate voltage region, space charge limited ($I \propto V^2$) and at still higher voltage thermionic emission ($I \propto V^3$) conduction mechanisms. In order to analyse these curves (figure 3), we apply the model proposed by Rose [22] for defect insulators containing shallow traps. According to this model space charge limited (SCL) current is given by

$$I = \frac{9}{8}\frac{\mu_c \varepsilon V^2}{d^3}, \tag{1}$$

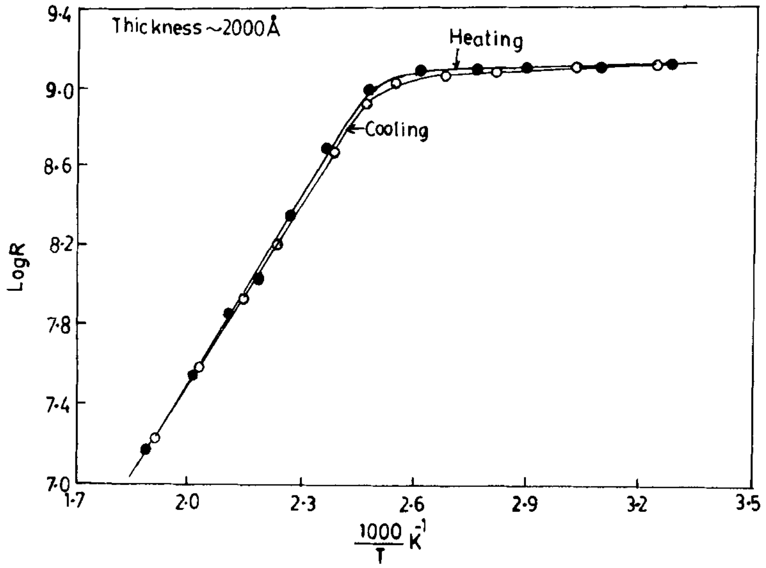

Figure 2. Log R vs $1/T$ for AgCl film of thickness ~ 2000 Å.

Table 1. ΔE values of AgCl films.

Thickness d (Å)	ΔE (eV) From resistance measurements	Thickness d (Å)	ΔE (eV) from capacitance measurements
2201	0·675	1958	0·690
2574	0·631	2314	0·649
2788	0·614	2812	0·583
3412	0·584	3210	0·566
3615	0·561	3539	0·539

where V is the applied voltage, d, the sample thickness, μ_c, the effective drift mobility of charge carriers in the presence of shallow traps, and ε is the dielectric constant of the material. In the present investigation SCL current has been found to vary directly with V^2 (figure 3) and inversely with d^3 (figure 4). It is also known that [23, 24], the voltage at which the transition from ohmic to SCL conduction occurs (V_{trans}) is

$$V_{\text{trans}} = \frac{8}{9}\frac{e n_t d^2}{\varepsilon} \tag{2}$$

where n_t is the density of trapped carriers and other symbols have their usual meanings. In the present investigation, it has been found that V_{trans} is directly proportional to d^2 (figure 5). The constant value of energy of activation ($\Delta E \sim 0{\cdot}17$ eV) obtained from slopes of linear plots of $\log I$ versus $1/T$ (figure 6) suggests that energy level of traps to which the charge carriers are injected from electrodes does not vary with the applied field and the contact keeps injecting carriers all the time, which is the prerequisite for SCL currents [25]. At higher voltages where $I \propto V^3$, conduction process is emission limited. This is the break away region preceding the break down.

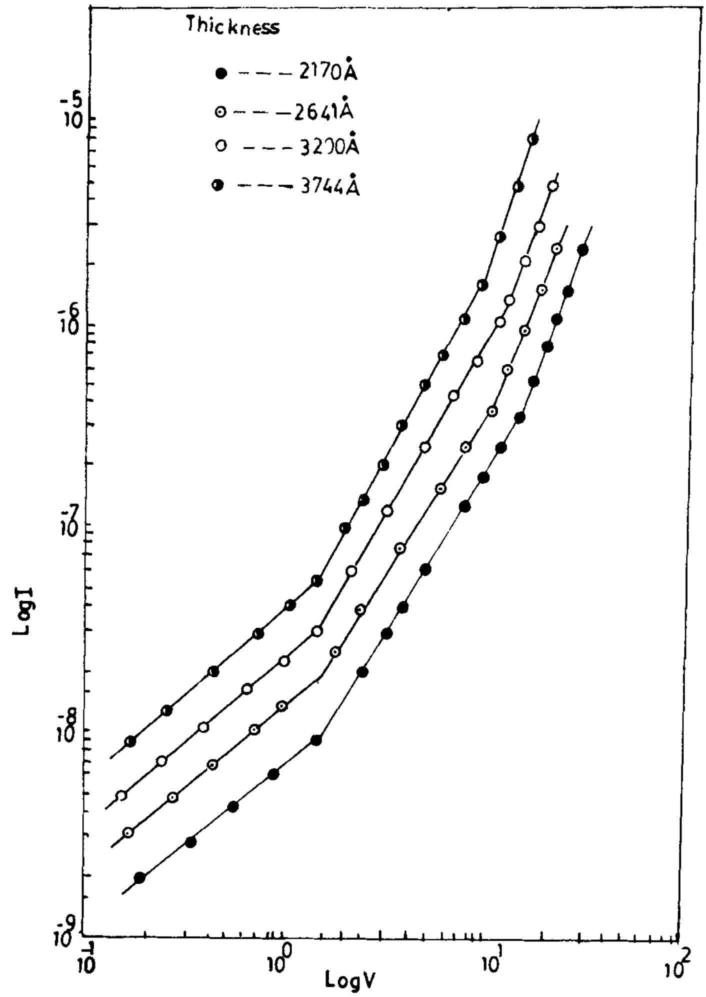

Figure 3. Log I vs log V for AgCl films at room temperature.

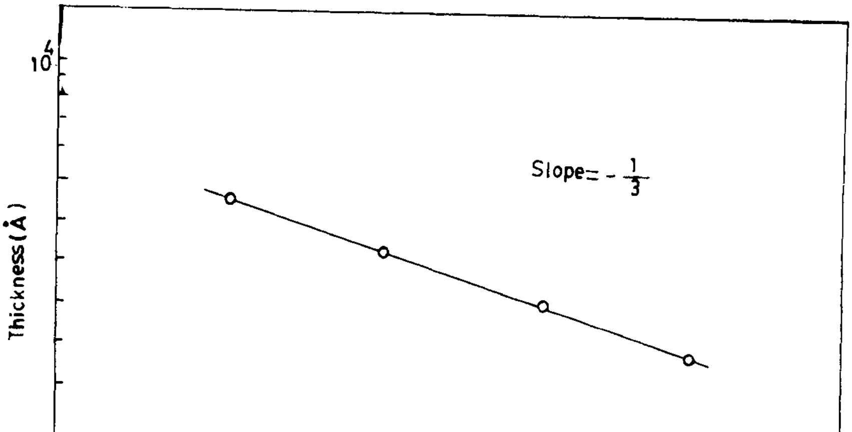

Figure 4. Log I vs d.

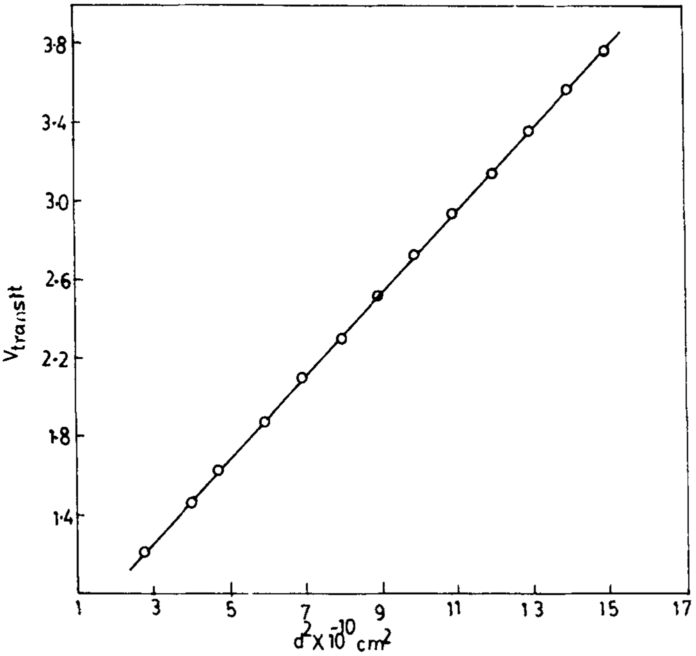

Figure 5. V_{trans} vs d^2.

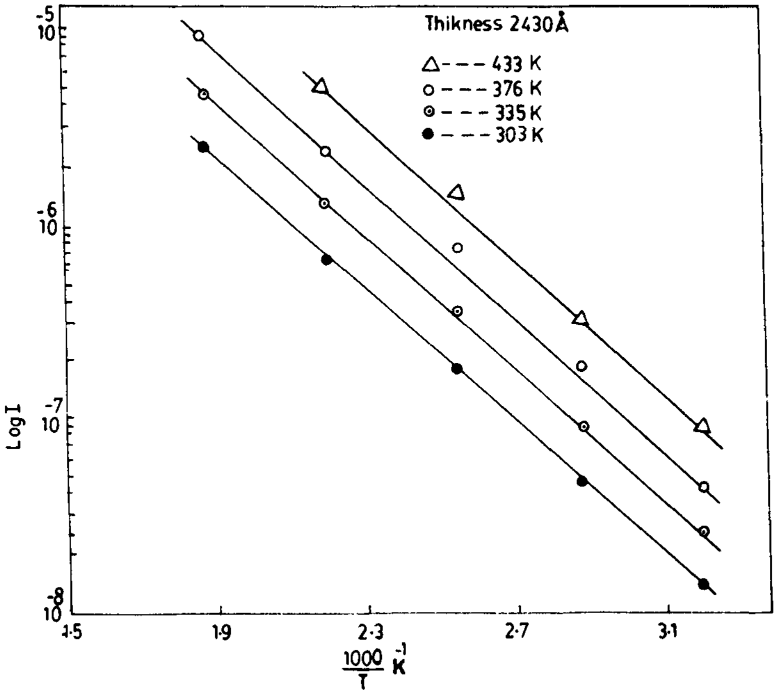

Figure 6. Log I vs $1/T$.

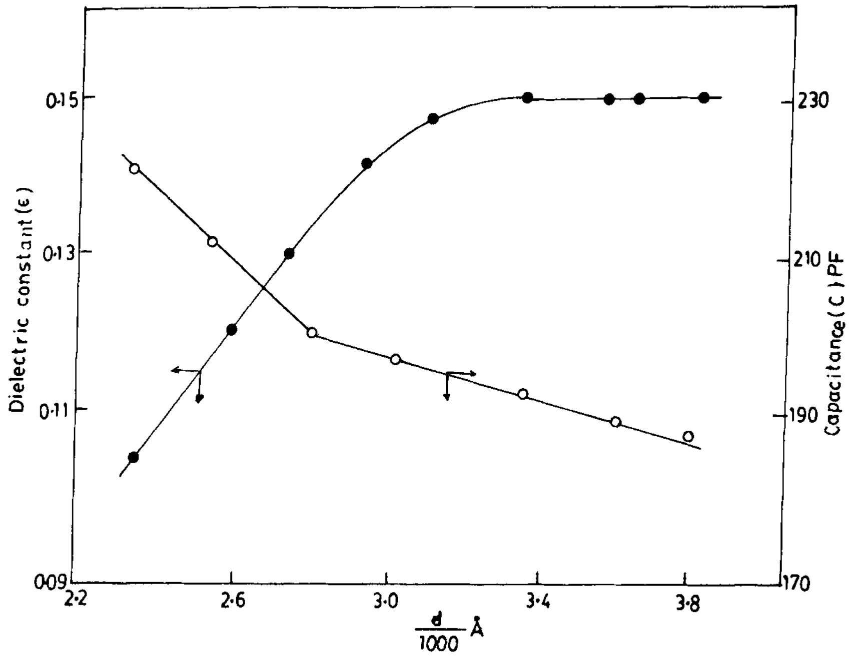

Figure 7. Capacitance and dielectric constant vs thickness.

Figure 7 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 later on attains a constant value ~ 0.15 at $d \sim 3200$ Å.

The values of C, ε, d, area (A) of the film and free space permitivity (ε_0) are interrelated by an equation [26]

$$C = \frac{\varepsilon\varepsilon_0 A}{d}. \tag{3}$$

Higher values of C at lower thickness can be attributed to a contribution to capacitance from a thin native oxide layer that is present on the lower aluminium electrode [27]. The increase of ε with increase of thickness can be related to the influence of grain size on dielectric constant. Grain size increases with thickness and dielectric constant increases with grain size and hence with thickness [28].

Since the dielectric constant is the material property, whereas capacitance is geometry dependent, the following interpretation would be the terms of ε and $\tan\delta$.

The variation of ε with f at various temperatures is presented in figure 8 for AgCl film of thickness 3800 ± 20 Å. In general, ε is found to decrease with frequency at all temperatures but this variation was less pronounced at lower temperatures. The manner in which ε varies with f, gives an indication as to which type of contribution is present [29]. The contribution from space charge polarization is mainly noticeable in the low frequency (0·01 Hz) region and depends on the purity and perfection of the films. In contrast, dipole orientation polarization can be exhibited by materials even up to 10^{10} Hz and is characterized by a Debye-type peak in the dielectric loss, while electronic and ionic polarization always exists below 10^{13} Hz. Since no relaxation effect (no $\tan\delta_{\max}$) is observed in the frequency and temperature regions studied, the

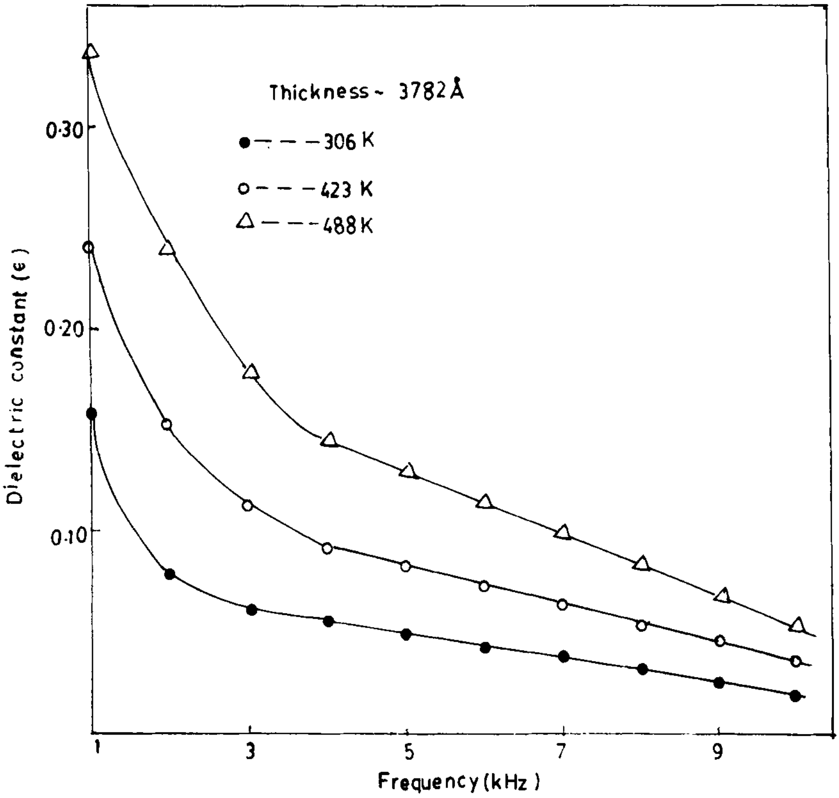

Figure 8. Dielectric constant vs frequency for a film of thickness ~ 3782 Å.

contribution from orientational polarization and possibly also that from interfacial polarization can be ruled out. Therefore only electronic and ionic polarizations contribute.

The most significant features of the ac behaviour of the AgCl film capacitors are the loss minimum ($\tan\delta_{\mathrm{min}}$) in the frequency curve and its shift to higher values and to higher frequencies with increasing temperature and vice-versa (figure 9). This is true for all films. The appearance of the loss minimum in the $\tan\delta$ versus frequency curve is attributed to the effect of lead resistance. Goswami and Goswami [30] have proposed a parallel resistor-capacitor model in which an ideal capacitor element of capacitance C, independent of frequency and temperature is in parallel with a dielectric resistive element of R and in series with a small lead resistance r, such that $R \gg r$. The frequency at which $(\tan\delta)_{\mathrm{min}}$ occurs is

$$\omega_{\mathrm{min}} = 2\pi f_{\mathrm{min}} = \frac{1}{C(rR)^{1/2}}, \tag{4}$$

where ω is the angular frequency and R is

$$R = R_0 \exp\left(\frac{\Delta E}{kT}\right). \tag{5}$$

Here R_0 is a constant and ΔE is the activation energy. Thus R would decrease when

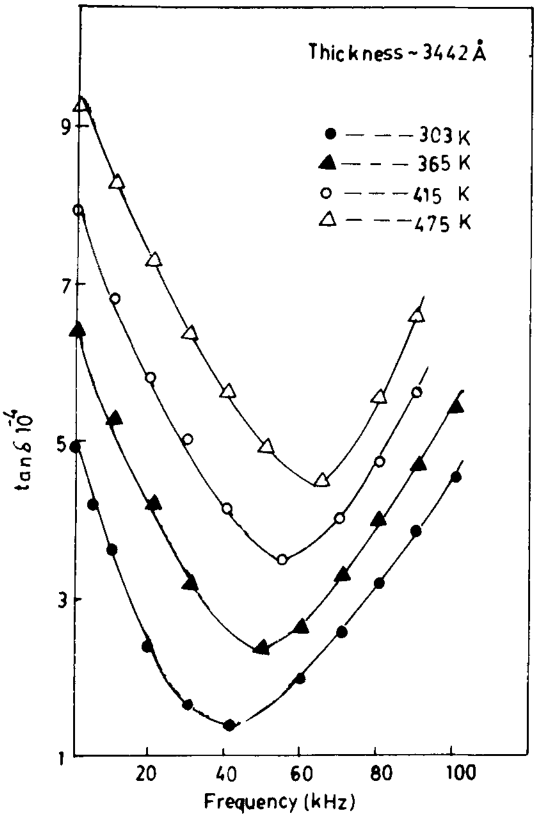

Figure 9. Tan δ vs frequency for a film of thickness ~ 3442 Å.

the temperature is raised and as a result $f_{\min}$ would shift towards the higher frequency region with rise in temperature. Recently Hino *et al* [27] proposed a capacitor model containing a capacitor with capacitance C and conductance σ. According to this model the minimum of $\tan\delta$ appears at the frequency ($f_{\min}$), satisfying the following relation

$$\omega_{\min}^2 = (2\pi f_{\min})^2 = \frac{\sigma(1 + R\sigma)}{C^2 R}. \tag{6}$$

Here R is the electrical resistance of native oxide layers formed on bottom Al electrodes. Since σ considerably increases with increase of temperature, R remaining practically unchanged, $f_{\min}$ will also be higher at high temperatures. Thus a shift of $f_{\min}$ would be to a higher frequency at higher temperatures and vice versa.

Figures 10 and 11 show variation of ε and $\tan\delta$ with temperature respectively. The values of ε and $\tan\delta$ increase with increase of temperature at all frequencies.

The temperature has a complicated influence on ε and $\tan\delta$, which in turn depend on electronic and ionic polarisation, dipole orientation polarisation, space charge polarisation etc. It may be pointed out that the dielectric conductivity is proportional to $\tan\delta$. Thus, as the temperature increases, the conductivity of the film and hence $\tan\delta$ would increase. The large increase of ε and $\tan\delta$ beyond 373 K may be assigned to ionic motion in the form of dipolar orientation.

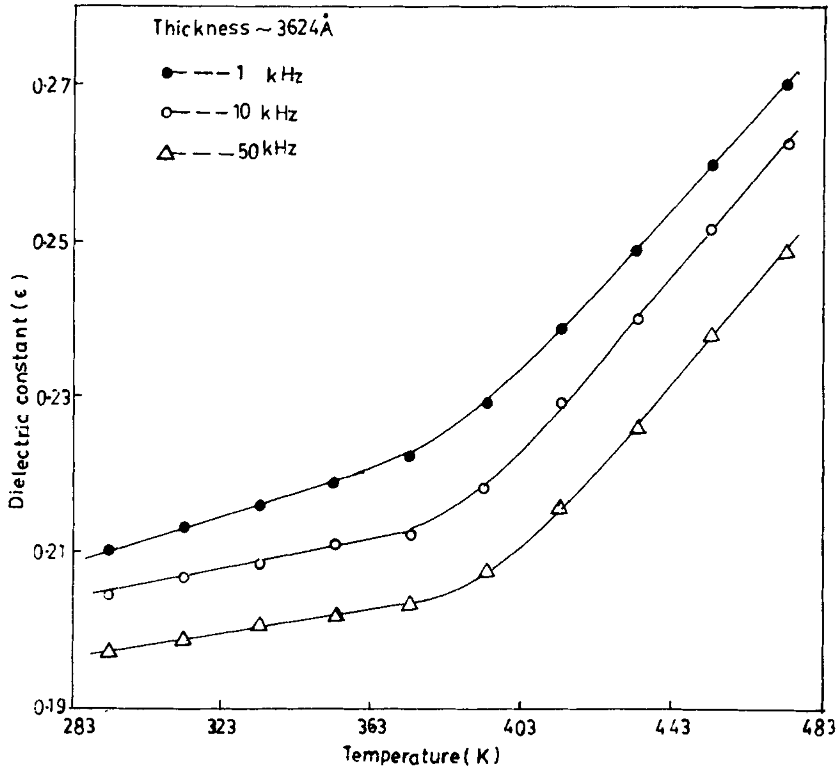

Figure 10. Dielectric constant vs temperature for a film of thickness ~ 3624 Å.

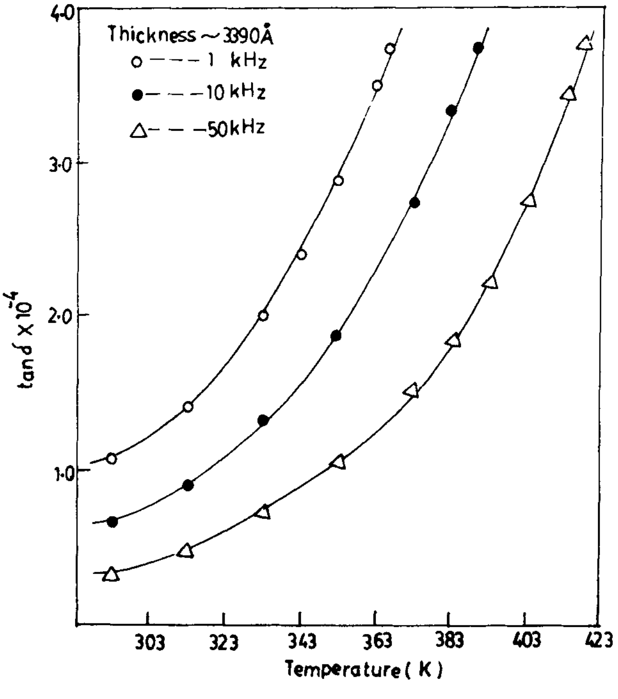

Figure 11. Tan δ vs temperature for a film of thickness ~ 3390 Å.

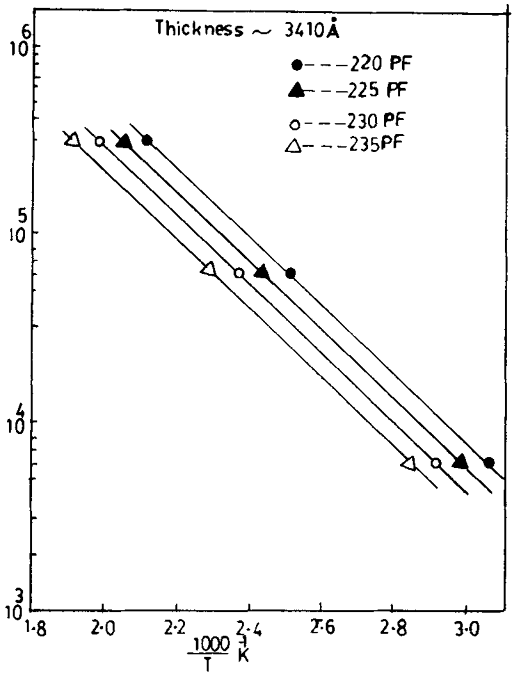

Figure 12. Log ω vs $1/T$ for a film of thickness ~3410 Å.

Therefore it can be said that in AgCl films major contributions to ε and $\tan\delta$ arise from the electronic and more probably from the ionic polarization due to the ionic nature of AgCl films.

According to Simmons *et al* [31] for any capacitor system with an inherent resistance, R_0,

$$\omega = 2\pi f = AR_0 \exp\left(\frac{-\Delta E}{kT}\right). \tag{7}$$

A is a constant whose magnitude depends on the particular selected value of constant capacitance. The variation of $\log\omega$ with $1/T$ for four constant capacitances for a film of thickness 3410 Å is represented in figure 12. The plots are found to be linear and parallel. Activation energies thus obtained from figure 12 are included in table 1 for comparison with those calculated from resistance measurements (figure 2). It is seen that ΔE from ε measurements and from resistance measurements are more or less identical.

4. Conclusions

Based on the experimental data presented and theoretical models discussed in this paper, it is concluded that amorphous AgCl films formed by using solution-gas interface technique are broad-band semiconductors exhibiting SCL and thermionic emission currents. Dielectric properties of these films indicate electronic and ionic polarization effects.

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