DETERMINATION OF DIELECTRIC CONSTANT OF STEARIC ACID FILMS USING VARYING GAP IMMERSION METHOD

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The dielectric constant data (at 3.5 MHz) on stearic acid thin films, obtained by using variable gap immersion method, are presented. Many of the errors of the conventional universal bridge method are eliminated in the method used here. It is also shown that the varying gap immersion method serves as an experimental tool for simultaneous determination of film thickness with high degree of accuracy. The data on evaporated as well as Langmuir films of stearic acid (≥1000 Å) are found to be consistent and in reasonable agreement.

1. INTRODUCTION

The rapid development of thin film technology and increasing demand for dielectric thin films in the microelectronics industry requires that their dielectric constant be determined accurately at high frequencies. There has been considerable progress to meet the industrial demands for measurement of dielectric parameters of various synthetic materials to be used in submarine cables at high frequencies, and the efficient systems developed are accurate up to 100 MHz. However, these systems could only be used to determine dielectric constant or loss tangent of sheet specimens several microns thick.

Most dielectric measurements on thin films, on the other hand, have been made using a conventional type universal LCR bridge which yields ε values with an accuracy in its own right. Nevertheless, this method of measurement suffers from some inherent practical problems. For example, the accurate knowledge of the film thickness and of the sandwiched area of the film are prerequisites of this method. The commonly used method of obtaining a wide variety of dielectric films is thermal evaporation in vacuum. Thickness of these films is directly estimated using a quartz crystal thickness monitor. Too much reliance cannot be laid on the accuracy of film thicknesses so obtained, and hence the ε values. If one measures film thicknesses optically, it involves additional time and labor. The bridge method is also insensitive for high frequency dielectric measurements.

To resolve most of the practical sources of errors, we have used the varying gap immersion method for measuring high frequency ε of thin films ≥1000Å. This method has been shown to give the most accurate determination of dielectric parameters of sheet specimens. One significant feature of this method is that it does not require knowledge of film thickness, but serves as a tool for obtaining film thickness. The measurements here have been made using an assembly of two parallel electrodes in conjunction with a highly sensitive and stabilised reactivity meter designed on the principle proposed earlier by one of the authors. A standard variable capacitor is also used to record small changes in the capacitance when the film sample is introduced between the electrodes.

The dielectric constant measurements on stearic acid thin films at 3.5 MHz are presented here. We have chosen this organic material, because it can be obtained in thin film form, both, by thermal evaporation in vacuum and by Blodgett-Langmuir technique.
Since the thicknesses of the films obtained in the latter technique are very accurately known, it offers a unique opportunity to test the suitability of varying gap immersion method for film thickness determination and ensures the reliability of the method, equipment and circuitry used for our measurements. No additional data, other than that obtained for \( \varepsilon \) determination, is needed for thickness calculations. Evaporated films of stearic acid have not been used before for such measurements.

2. THEORY

The following are the notations used, unless otherwise defined specifically, in the text:

- **A** = Area of the high potential electrode.
- **C** = Capacitance
- **\( \varepsilon \)** = Dielectric constant
- **\( T \)** = Spacing between the electrodes
- **\( \Delta C \)** = Change in capacitance
- **\( \Delta T \)** = Change in spacing
- **\( t \)** = Thickness

The suffixes used with the above notations correspond to the following:

- \( a \) = air; \( l \) = liquid; \( s \) = substrate and \( f \) = film.

2.1. For Dielectric Constant

For the initial air gap \( T_a \), the capacitance of the electrode system is

\[
C_a = \frac{\varepsilon_a A}{T_a} \tag{1}
\]

On insertion of the bare substrate between the electrodes, the capacitance of the system, \( C_{as} \), is

\[
C_{as} = \frac{C_a}{1 - \lambda_a [1 - (1/\varepsilon_s)]} \tag{2}
\]

where \( \lambda_a = t_s/T_a \). Similarly, if the air medium is replaced by the liquid, keeping \( T_a \) constant, the respective capacitance values of the electrode system without and with the substrate are given by

\[
C_l = \frac{\varepsilon_a \varepsilon_l A}{T_a} \tag{3}
\]

\[
C_{ls} = \frac{C_l}{1 - \lambda_l [1 - (1/\varepsilon_s)]} \tag{4}
\]

From Eq. (2)

\[
1 - \lambda_a (1 - \frac{1}{\varepsilon_s}) = \frac{C_a}{C_{as}} = \frac{C_a}{C_a + \Delta C_{as}}
\]

\[
= \frac{1}{1 + (\Delta C_{as}/C_a)} \tag{5}
\]

where \( \Delta C_{as} \) is the change in capacitance on substrate insertion in an air medium. Similarly, if \( \Delta C_{ls} \) represents capacitance change in the liquid medium and \( \varepsilon_s > \varepsilon_l \); from Eq. (4)

\[
1 - \lambda_l (1 - \frac{\varepsilon_l}{\varepsilon_s}) = \frac{C_l}{C_{ls}} = \frac{1}{1 + (\Delta C_{ls}/C_l)} \tag{6}
\]

If the film specimen \((t_f, \varepsilon_f)\) deposited on the substrate \((t_s, \varepsilon_s)\) is now inserted first in the air medium and subsequently in the liquid medium (the spacing between the electrodes \( T_a \) is held constant), the respective capacitance changes are given by

\[
\Delta C_{af} = \frac{C_a \lambda_f [1 - (1/\varepsilon_f)]}{\{1 - \lambda_s [1 - (1/\varepsilon_s)]\} \{1 - \lambda_f [1 - (1/\varepsilon_s)]\} - \lambda_f [1 - (1/\varepsilon_f)]} \tag{7}
\]

and

\[
\Delta C_{lf} = \frac{C_l \lambda_f [\varepsilon_l/\varepsilon_f - 1]}{\{1 - \lambda_s [1 - (\varepsilon_l/\varepsilon_s)]\} \{1 - \lambda_s [1 - \varepsilon_l/\varepsilon_s] + \lambda_f [\varepsilon_l/\varepsilon_f - 1]\}} \tag{8}
\]

Eq. (8) is valid for \( \varepsilon_f < \varepsilon_l \). Readjusting Eq. (7) and combining with Eq. (5), we obtain

\[
\frac{\Delta C_{af}}{C_a} \left\{1 - \lambda_s [1 - \frac{1}{\varepsilon_s}]\right\}^2 = \lambda_f \left[1 - \frac{1}{\varepsilon_f}\right] \left[1 + \frac{\Delta C_{af}}{C_{as}}\right] \tag{9}
\]

Similarly, from Eq.'s (6) and (8):

\[
\frac{\Delta C_{lf}}{C_l} \left\{1 - \lambda_s [1 - \frac{\varepsilon_l}{\varepsilon_s}]\right\}^2 = \lambda_f \left[\frac{\varepsilon_l}{\varepsilon_f} - 1\right] \left[1 - \frac{\Delta C_{lf}}{C_{ls}}\right] \tag{10}
\]

Dividing Eq. (10) by Eq. (9); substituting the parameters \( X, Y \) and \( Z \) as defined below and rearranging, we have

\[
\varepsilon_f = \frac{\varepsilon^2 Y + XZ}{\varepsilon_l Y + XZ} \tag{11}
\]
where

\[ e_l = \frac{C_l}{C_a} \quad ; \quad X = \frac{\Delta C_{lf}}{\Delta C_{af}} \]  \hspace{1cm} (12)

\[ Y = \left( \frac{1 - \lambda_s \left[ 1 - (1/\epsilon_s) \right]}{1 - \lambda_s \left[ 1 - (\epsilon_l/\epsilon_s) \right]} \right)^2 \]

\[ Z = \left[ \frac{1 + \Delta C_{af}/C_{as}}{1 - \Delta C_{af}/C_{ls}} \right] \]

If the film thickness is small \(\ll 10^4 \text{Å} \), \(Z = 1 \) because,

\[ \frac{\Delta C_{af}}{C_{as}} \ll 1 \quad \text{and} \quad \frac{\Delta C_{lf}}{C_{ls}} \ll 1 \]

Therefore,

\[ e_f = \frac{e_l^2 Y + X}{e_l Y + X} \]  \hspace{1cm} (13)

when \(e_f < e_l \) and \(e_s > e_l \).

However, if \(e_f > e_l \) and \(e_s > e_l \), the expression for \(e_f \)

obtained in the same way and given by

\[ e_f = \frac{e_l^2 Y - X}{e_l Y - X} \]  \hspace{1cm} (14)

where \(X\) and \(Y\) are the same as defined in Eq. (12).

For the case, when \(e_f < e_l \) and \(e_s < e_l \), the expression obtained is

\[ e_f = \frac{e_l^2 Y + X}{e_l Y + X} \]  \hspace{1cm} (15)

where

\[ X = \frac{\Delta C_{lf}}{\Delta C_{af}} \]

and

\[ Y = \left( \frac{1 - \lambda_s \left[ 1 - (1/\epsilon_s) \right]}{1 + \lambda_s \left[ (\epsilon_l/\epsilon_s) - 1 \right]} \right)^2 \]

Evidently, the expressions (13), (14) and (15) are independent of the film thickness or film area values, and simply demand the accurate experimental determination of \(\Delta C_{af}\) and \(\Delta C_{lf}\). All other parameters involved are known.

2.2. For Film Thickness

From Eq. (9),

\[ t_f = T_a \left( \frac{\Delta C_{af}/C_a}{\frac{1}{(1 - (1/\epsilon_f))} \left[ 1 + (\Delta C_{af}/C_{af}) \right]} \right)^2 \]

Combining the above with Eq. (5) and since \(\Delta C_{af}/C_{as} \ll 1\), we obtain,

\[ t_f = T_a \frac{\Delta C_{af}}{C_a} \left[ 1 + (\Delta C_{af}/C_{as}) \right]^2 \frac{1}{1 - (1/\epsilon_f)} \]  \hspace{1cm} (16)

Thus the expression for \(t_f\) does not demand any additional parameters to be measured experimentally. The term \(1 + (\Delta C_{af}/C_{as})\) is calculated using Eq. (5) in which all the values are known.

3. EXPERIMENTAL

The varying gap immersion method involves measurement of capacitance changes when the film sample is inserted between the electrodes in (i) an air medium, and (ii) a medium of a liquid of known dielectric constant. The measurements here have been made using an assembly of two parallel electrodes, namely, the upper high potential (fixed) and the lower earth potential (movable), with their respective diameters 20 mm and 35 mm. The shift of the lower electrode was read by a micrometer (least count = 0.5 micron), attached to the assembly mechanically. The reactance meter coupled to the electrode assembly was designed on the principle proposed earlier, and had high sensitivity (\(\approx 15 \mu\text{A}/10^{-3}\text{pF}\)) and stability. It was used in conjunction with a quartz crystal oscillator at high frequency (3.5 MHz). A micro-ammeter used in its detector circuit enabled direct capacitance measurements to be made in terms of the current flowing in the circuit. Since the respective capacitance changes, both in air and liquid, were too small, they were directly obtained by using a standard variable capacitor across the electrode assembly.

The two important requirements of the method used here are that (i) the specimen (with or without film) of exactly the same area and thickness should always be placed against the earth potential electrode in exactly the same position, and (ii) the liquid used should have nearly the same dielectric constant as that of the material under investigation. In our experiments, for each set of measurements two glass specimens (25 x 25 mm²) were carefully cut from the same slide to ensure exactly the same thickness and dielectric constant. One of them was used as a
reference substrate \( (t_s, \varepsilon_s) \), and the other for film deposition. A guide was provided on the earth potential electrode to satisfy the requirement that the slide occupies the same position every time. The silicon liquid used as the reference liquid had a dielectric constant \( \varepsilon_s = 2.31 \) at 20°C. This was measured very accurately by 4-terminal method using a liquid cell. The dielectric constant of the glass substrate was determined beforehand by the gap variation method in each set of measurements.

Stearic acid films in the thickness range 100 Å to 3500 Å were evaporated in a conventional vacuum coating unit following the method described elsewhere. Their film thicknesses were estimated by coupling a quartz crystal monitor to the evaporator. In the case of Blodgett-Langmuir process, the technique used was the same as described earlier, except that no salts, such as BaCl\(_2\), were dissolved in the distilled water as we were interested to obtain pure fatty acid films. The trough being small (29 x 20 x 6 cm\(^3\)), we could obtain good quality films containing as many as 61 layers (≈1525 Å) only. The thickness of these films were directly obtained by multiplying the number of deposited layers by the monolayer thickness (≈25 Å).

In the actual method of measurements, first the resonance condition in the reactance meter was obtained by following the operations reported earlier. Next, the output current in the micro-ammeter was reduced to zero when the reference glass specimen was inserted between the electrodes, separated by an initial air gap \( T_a = 1.2 \) mm. Subsequently, the substrate was removed and the earth potential electrode was moved to restore the zero output of the reactance meter. The electrode shift \( \Delta T \), so obtained by the micrometer, was used to calculate \( \varepsilon_s \) using the following equation,

\[
\varepsilon_s = \frac{t_s}{t_s - \Delta T}
\]

The reference substrate was placed back in its initial position and the zero output was obtained once again keeping \( T_a = 1.2 \) mm. Now, the reference was replaced by the film specimen and this time the zero output was brought back using the standard variable capacitor which is a direct measure of the change in capacitance due to film in air medium (\( \Delta C_{air} \)). The whole process was repeated once again replacing the medium by liquid (silicon) and the required value of \( \Delta C_{film} \) was obtained. The values of \( \varepsilon_f \) and \( t_f \) were calculated using Eqs. (14) and (16), respectively. The predetermined \( \varepsilon \) values of evaporated stearic acid films (\( \varepsilon \approx 2.7 \)) obtained by the universal bridge method led us to use the Eq. (14) because \( \varepsilon_f \) is clearly greater than \( \varepsilon_l (= 2.31 \) for silicon liquid).

4. RESULTS AND DISCUSSION

The results obtained both on Langmuir and evaporated films of stearic acid are summarised in Tables I and II, respectively. All the notations used in the tables have the same significance as described earlier. Since the diameter of the high potential electrode is 20 mm, the capacitance of the electrode assembly in air \( C_a \) used in our calculations was 2.315 pF. Reports of dielectric data on Langmuir films using various types of measuring methods are reviewed elsewhere. Khanna and coworkers obtained \( \varepsilon \) values of barium stearate both theoretically and experimentally (by universal bridge method). The respective values thus obtained for multilayer (thick) barium stearate were 3.10 (theory) and 2.63 (experimentally). The arguments given by these workers accounting for the discrepancy between these values still stand valid. To our knowledge, no one has reported similar data on stearic acid films which differ in structure as well as in the dielectric behaviour compared to Ba-stearate films. The former are monoclinic whereas the latter possess h.c.p. The metal ions (Ba\(^{++}\)) contained by the latter contribute to the dielectric polarizability and reduce the mobility of polar groups by linking one molecule with another (cf. Ref. 6, p. 17).

Therefore, no quantitative comparison can be made between our data and that of earlier workers. Nevertheless, the reliability of the method used and the accuracy of results can be established by the fact that \( \varepsilon \) values obtained, in the given thickness range, are consistent. Further, a very good agreement between the calculated and known thickness values (column 10 and 11 in Table I) of Langmuir films gives an added support. The maximum discrepancy is only 1.4%. In the case of evaporated films (Table II), a similar comparison between thicknesses is not equally meaningful because the known values (column 11) were determined by crystal thickness monitor. The latter is a relative method involving density of the material and frequency difference. Some qualitative justification to our \( \varepsilon_f \) values may also be assigned in terms of the known values of refractive index of Ba-stearate films \( (n = 1.55) \) as reported by Lucy. Withholding the validity of Maxwell relation \( \varepsilon_{in} = n^2 \), the dielectric constant at optical frequencies \( (\varepsilon_{in}) \) is 2.42. The discrepancy
# TABLE I

Dielectric constant and thickness data on Langmuir films of stearic acid. The numerical number following LF– in the first column indicates the number of transferred monolayers on the slide.

| Sample | \( t_s \) mm | \( \varepsilon_s \) | \( \Delta C_{af} \times 10^3 \) pF | \( \Delta C_f \times 10^3 \) pF | \( \Delta C_{as}/C_a \) | \( X \) | \( Y \) | \( \varepsilon_f \) | \( t_f \) (calc.) A | \( t_f \) (exp.) A | Error % |
|--------|------------|----------------|-----------------|------------------|------------------|---|---|---|-------------|-------------|--------|
| LF–61  | 1.080      | 7.4742         | 3.8067          | 0.70             | 3.5372           | 0.1839 | 0.3394 | 2.71 | 1518        | 1525        | 0.46   |
| LF–57  | 1.080      | 7.4742         | 3.56            | 0.65             | 3.5372           | 0.1826 | 0.3394 | 2.71 | 1421        | 1425        | 0.28   |
| LF–51  | 1.086      | 7.5417         | 3.403           | 0.61             | 3.6512           | 0.1793 | 0.3335 | 2.71 | 1293        | 1275        | 1.40   |
| LF–47  | 1.084      | 7.5541         | 3.055           | 0.56             | 3.6232           | 0.1833 | 0.3363 | 2.72 | 1173        | 1175        | 0.17   |
| LF–41  | 1.086      | 7.5417         | 2.702           | 0.49             | 3.6512           | 0.1813 | 0.3335 | 2.71 | 1025        | 1025        | nil    |

# TABLE II

Dielectric constant and thickness data on evaporated films of stearic acid.

| Sample | \( t_s \) mm | \( \varepsilon_s \) | \( \Delta C_{af} \times 10^3 \) pF | \( \Delta C_f \times 10^3 \) pF | \( \Delta C_{as}/C_a \) | \( X \) | \( Y \) | \( \varepsilon_f \) | \( t_f \) (calc.) A | \( t_f \) (exp.) A | Error % |
|--------|------------|----------------|-----------------|------------------|------------------|---|---|---|-------------|-------------|--------|
| SA–9   | 1.085      | 7.60           | 7.19            | 1.45             | 3.6554           | 0.2017 | 0.3340 | 2.77 | 2700        | 2720        | 0.74   |
| SA–10  | 1.085      | 7.60           | 4.51            | 0.91             | 3.6554           | 0.2018 | 0.3340 | 2.76 | 1691        | 1700        | 0.53   |
| SA–14  | 1.09       | 7.5437         | 3.85            | 0.76             | 3.7148           | 0.1974 | 0.3286 | 2.77 | 1405        | 1360        | 3.31   |
| SA–15  | 1.085      | 7.55           | 4.05            | 0.90             | 3.6384           | 0.2     | 0.3348 | 2.77 | 1699        | 1700        | 0.06   |
| SA–16  | 1.085      | 7.55           | 6.85            | 1.38             | 3.6384           | 0.2013 | 0.3348 | 2.77 | 2583        | 2550        | 1.3    |
| SA–17  | 1.08       | 7.5262         | 8.8             | 1.80             | 3.5538           | 0.3432 | 0.3401 | 2.77 | 3441        | 3400        | 1.21   |
| SA–18  | 1.08       | 7.5262         | 2.703           | 0.55             | 3.5538           | 0.2035 | 0.3401 | 2.77 | 1058        | 1020        | 3.73   |
between $\varepsilon_{\text{me}}$ and $\varepsilon_f$ is physically conceivable because of the significant difference in the measurement frequencies. It has been shown earlier that at measurement frequencies as high as $10^2$ to $10^{10}$ MHz, the measured values of dielectric constant of non-polar polystyrene-like materials differ from their corresponding $n^2$ values ($\varepsilon = 2.55$ and $n^2 = 2.53$).\textsuperscript{12} The stearic acid also behaves as a nominally non-polar material.

The discrepancy in the $\varepsilon$ values of two types of films is attributed to factors, such as the relative unevenness of the evaporated films as against the uniformity of Langmuir films and to a certain extent, to the presence of moisture content in the latter. However, the Langmuir films were stored in a dry atmosphere prior to the dielectric measurements. The implications of other experimental errors are also important in the whole range of data given here.

As a final remark, the significant feature, leading to the versatility of the varying gap immersion method, is the possibility of simultaneous and accurate determination of dielectric constant and film thicknesses. The stray capacitance effects are completely eliminated. This method, in principle, can also be used to measure the dielectric losses with a similar high degree of accuracy. The only essential requirement for such measurements is to use a loss detector to obtain parallel equivalent resistance. Since evaporated films of fatty acids are of relatively recent origin, further dielectric studies will help to resolve many difficulties arising in the case of Langmuir films (discussed in Ref. 6). The practical applications of such films in the field of tribology for lubrication\textsuperscript{13} and in the investigations of fingerprint thin films\textsuperscript{14} are already known.

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REFERENCES

1. A. Kakimoto and B. Ichijo, \textit{IEEE Trans. Plts. Mats. Packag.}, PMP-6 (1970) 106.
2. B. Ichijo and T. Arai, \textit{Rev. Sci. Instrum.}, 32 (1961) 122.
3. V. K. Agarwal, Y. Igasaki and H. Mitsuhashi, \textit{Thin Solid Films}, 33 (1976) L31.
4. K. B. Blodgett and I. Langmuir, \textit{Phys. Rev.}, 51 (1937) 946.
5. H. Ichimura, A. Kakimoto and B. Ichijo, \textit{IEEE Trans. Plts. Mats. Packag.}, PMP-4 (1968) 35.
6. V. K. Agarwal, \textit{Electrocomp. Sci. and Technol.}, 2 (1975) 1.
7. U. Khanna, V. K. Srivastava and V. K. Agarwal, \textit{Thin Films}, 2 (1972) 83.
8. U. Khanna and V. K. Srivastava, \textit{Thin Films}, 2 (1972) 167.
9. U. Khanna and V. K. Srivastava, \textit{Thin Solid Films}, 12 (1972) S25.
10. L. H. Germer and K. H. Storks, \textit{J. Chem. Phys.}, 6 (1938) 280.
11. F. A. Lucy, \textit{J. Chem. Phys.}, 16 (1948) 167.
12. L. Hartshorn and J. A. Saxton, \textit{Handbuch der Physik}, 16 (1958) 640.
13. M. A. Baker, \textit{Thin Solid Films}, 8 (1971) R 13.
14. G. L. Thomas, \textit{Thin Solid Films}, 24 (1974) S 52.
