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THICK FILM PASTE PREPARATION AND CHARACTERIZATION OF $BaTiO_3$ FOR HUMIDITY SENSOR

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ABSTRACT

A dielectric material of $BaTiO_3$ powder was prepared using solid state reaction from raw materials; $BaCO_3$ and TiO_2. A study was conducted to prepare the $BaTiO_3$ thick film paste by mixing the organic vehicle and the sintered powder in ratio of 30:70. The organic vehicle was formed from suspending ethyl cellulose resins into terpineol solvent in a specific ratio. The paste was printing onto ceramic substrate by using DEK J1202 thick film screen printer machine. The recipe and the process in producing $BaTiO_3$ thick film paste was then established. The electrical properties of screen-printed $BaTiO_3$ were investigated in an interdigitated electrode pattern. Experimental results show that the smaller gap between two adjacent electrodes gives higher capacitance and lower resistance value, thus provide better response time in detecting capacitor changes for sensor application. An equivalent circuit to represent the dialectic mechanism of the $BaTiO_3$ thick film sample has also been established.

Keywords: *Screen printed sensor, Interdigitated electrode, complex capacitance, electrical resistivity*

INTRODUCTION

Thick film is preferred generic description for the field of microelectronics in which specially formulated pastes are applied onto a ceramic or insulating substrate [1]. The deposited paste with a desired pattern is then thermally treated in a furnace at high temperature to produce a set of passive component or sensing element. One common method to produce a thick film is by screen printing technique. This technique is relatively mature technology with a simple and convenient method to produce thicker layers up to 100µm [3] and the thickness of film is controllable. This process is useful to accommodate the demands of miniaturization, circuit complexity, multiplayer assemblers or high frequencies [4]. Besides, it has advantages over other method in term of cost production and complexity of machinery.

In screen printing fabrication, the paste is applied to the screen and the squeegee travels over the screen, pressing it down into contact with the substrate. The paste is force to go through the open areas of mesh-reinforced screen and thus deposited it onto the surface of a substrate [2]. After printing, the substrate is left at the room temperature or drying it with an infra-red drying system to allow the paste adhere to substrate before continuously printing next layer. In drying stage, the organic vehicles, which give the ink viscosity, are also been removed [2]. Next, the film is firing in a furnace at a relatively high temperature to remove remaining organic solvent and to fuse the films to the substrate. This process, which is know as sintering, also play important role for the electrical characteristic and the microstructure of the film by varying the peak firing temperature.

In screen printing process, the paste which is printing medium is the heart of the whole thick film fabrication. The paste is made from primary functional component (metal, metal-oxide, semiconductor or dielectric), which in powder form suspended in organic vehicles [1]. By changing the nature of the primary component of the paste, the characteristic of the film can be varied accordingly. Besides, the shape and size of the electrode structure also play an important role to enhance the sensitivities of the films characteristic [7]. Basically, meandering and interdigitation electrode pattern was used to maximize some property of whole structure in thick film sensor technology [1]. In general, the purpose of a meander structure is to maximize the total

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resistance, while interdigitated electrode pattern is to maximize the electrical admittance between two conducting structure.

In this experiment, the primary functional material used is a Barium Titanate ($BaTiO_3$) powder, prepared by solid state reaction. Through this method, the equimolar of the $BaCO_3$ and TiO_2 will be reacting at high temperature to form the $BaTiO_3$ powder. Next, the organic vehicles composition of terpineol solvent and cellulose resins is investigated and established. This solvent is used to form the screen printing paste when mixed with $BaTiO_3$ powder in ratio of 30:70 [5]. The paste is then deposited onto a ceramic substrate by screen printing technique. The electrical properties of the $BaTiO_3$ thick film were investigated.

MATERIALS AND METHODS

Powder Preparation

The stating materials for the $BaTiO_3$ powder are $BaCO_3$ and TiO_2. Equimolar amounts of the stating material were mixed and wet-ball milled in acetone for 24 hours, then dried in oven at 110°C. Next, the mixing powders were intermediate grinding before calcined at 3°C/minute to a temperature of 850°C and held for 24 hours, followed by cooling at 3°C/minute. After this procedure, the mixing powder was grinding to obtain fine grain particle size using pestle and mortal. The fine grain powder then sintered at 1000°C for 8 hours with ramping rate 3°C/minute for heating and cooling [8].

Organic Vehicle and Paste Preparation

A study was conducted to find the best ratio of organic vehicle between terpineol solvent and ethyl cellulose resins. The terpineol solvent was made by stirring α-terpineol (0.5g) into ethanol (30ml). The solution is then mixed with 0.25g of ethyl cellulose resins. A number of samples shown in Table 1 were used to establish the best form of paste. The ethyl cellulose was dissolved into terpineol solvent after one day left at room temperature. Next, the thick film paste was prepared by drop the organic vehicles wisely into $BaTiO_3$ powder by maintaining the ratio at 30:70. The mixture was mixed thoroughly to form homogenous paste by the 100 rpm magnetic stirrer at 40°C for about an hour.

Table 1: Different ratio of organic vehicle for paste preparation.

Samples	Ratio of terpineol solvent to ethyl cellulose
1	6:1
2	8:1
3	10:1
4	12:1
5	14:1

$BaTiO_3$ Thick Film Structure Design

The $BaTiO_3$ thick film structure is a two-layer device printed on a ceramic substrate as shows in Figure 1. The first layer is silver conductor paint and second layer is the $BaTiO_3$ film layer.

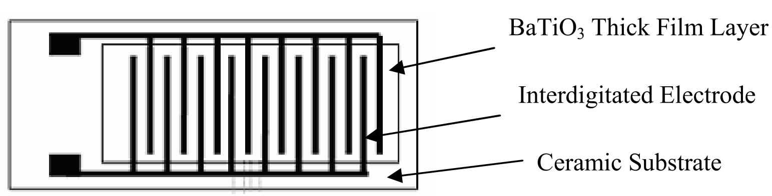

Figure 1: Layout of the $BaTiO_3$ Thick Film Structure

The $BaTiO_3$ film was deposited onto the total area occupied by the intedigited electrode. In general, the purpose of interdigitated electrode pattern is used to maximize the electrical admittance (capacitance or resistance) of

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material deposited over the electrode. In order to investigate the effect of interdigitated gaps to the dielectric properties of $BaTiO_3$ film, the design of electrode was varied as shows in Table 2. For the purpose of comparison, the samples were named as El 1, El 2 and El 3 accordingly.

The thick film screen printing was fabricated using DEK J1202RS automatic screen printing machine. First, the interdigitated electrode pattern was printing on the ceramic substrate. The printing electrode then was dried into belt dryer under Infra Red lamp at 150°C for 20 minute to dry the paste before going to the firing process in a furnace. The firing process is set at the peak temperature, 850°C for 10 minutes. Next, the $BaTiO_3$ thick film layer was overprinted onto the substrate with interdigitated electrode pattern. The similar drying and firing process was repeated for the $BaTiO_3$ layer.

Table 2: Design parameter for sample El1, El2 and El3 of screen printed $BaTiO_3$.

Samples	Gap length (mm)	Area of printed dielectric layer (mm^2)
El 1	0.2	48
El 2	0.6	72
El 3	0.8	96

Characterization of Thick Film $BaTiO_3$

The characterizations of the $BaTiO_3$ powder was made by Philips X-ray diffractometer (XRD) with Cu Kα (λ=1.542Å) radiation and the Bragg angle (2θ) ranging from 20º to 80º at room temperature. The electrical properties of the thick film $BaTiO_3$ were carried out in terms of capacitance and dc resistivity. The data for the complex capacitance analysis is obtained from ac measurement of capacitance, C, and conductance, G, as a function of frequency over the range of 10Hz to 10MHz using LCR meter (Hp 4126). The dc resistivity for the thick film sample was measured by two-point probe, semiconductor Measuring Unit (SMU), model Keithly 4200.

RESULTS AND DISCUSSION

The $BaTiO_3$ powders were produce by solid state chemical reaction based on $BaCO_3$ and TiO_2 as raw materials. The mixtures of raw material are in equimolar relation based on chemical reaction as given as follow [2]:

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \quad \text{.................(1)}$$

The resulting $BaTiO_3$ powder was examined by powder X-ray diffraction analysis with Cu-Kα radiation in the range 2ϴ=10° to 80° (ϴ=Brag angle) with a resolution of Δ2ϴ=0.03°.

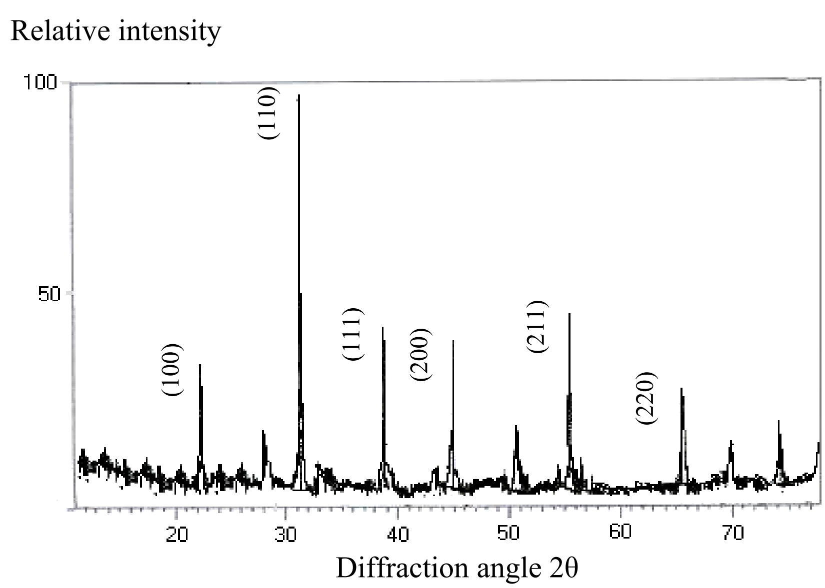

Figure 2: XRD pattern for $BaTiO_3$ powders.

From the graph pattern (Figure 2), the highest peak intensity is at 2θ=31.62°. The graphs pattern is almost same as reported by Niepce [9], which indicates that the powder is a $BaTiO_3$. To clearly identify, the plot graph was compared with the standard XRD stick pattern of Barium Titanate (provide by XRD software database) and show nearly same pattern indicating the $BaCO_2$ and TiO_2 are well combined to form $BaTiO_3$ powder.

The ratio of terpineol solvent to ethyl cellulose resins was varying as shows in Table 1. The mixture was pouring in the beaker with certain volume and weighted. The organic vehicles density, δ (g/mL) was calculated by following Equation:

$$\delta = W / V \text{ ……………………(2)}$$

Where W is the weight of the organic vehicle in gram and V is the volume of the organic vehicles in milliliter (ml). Figure 3 shows the plotting graph of the organic vehicles density versus samples.

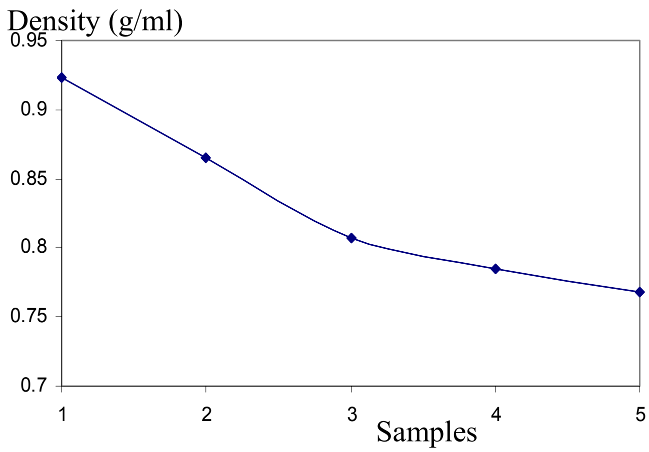

Figure 3: Organic vehicle density for the 5 samples

From Figure 3, sample 1 shows the highest density and the density of the organic vehicles reduces as the ratio of terpineol solvent was increased. The decreases in organic vehicle density made the solution become less viscous. Next, all the 5 samples are mixed with the $BaTiO_3$ powder in the ratio at 30:70 to form thick film paste. The mixer solution was stirrer by magnetic stirrer to form homogenous paste. After the stirring process, only sample 3, 4 and 5 show diluents properties for thick film screen printing procedure. Sample 1 and 2 were not diluents enough to be used as a thick film paste.

Fabrication of $BaTiO_3$ Thick Film

Samples 3, 4 and 5 pastes were screen printed onto the interdigitated electrode pattern in order to investigate the reliability of the thick film paste. The reliable paste must have properties such as good printing quality, fine line resolution and fast drying rate. The paste for sample number 3 with ratio of 10:1 for terpineol solvent to ethyl cellulose shows the fastest drying rate. The paste easily become dry on screen before screen printing process was made. This behavior makes the paste is not suitable for screen printing based on time factor in printing process. The paste for sample number 4 was better than sample number 3. The paste has been successfully screen printed with a good printing quality and fine line resolution on the interdigitaed electrode pattern. The number 5 sample shows more diluents compare to the sample number 4. Consequently, the drying rate for the sample number 5 becomes slower and the paste not sticks very well with the substrate after the printing process. Therefore, based on this study, the samples number 4 was suitable to be use as a recipe in thick film screen printing technique. The electrical properties of $BaTiO_3$ thick film for sample number 4 will be characterize with 3 different interdigitated electrode structures as shown by Table 2.

Electrical Properties of Thick Film $BaTiO_3$

Complex Capacitance Analysis

It is well known that the dielectric constant of the material is in proportional to the capacitance, so the dielectric property of the material can be investigated by means of the capacitance property. In general, the electrical properties of the material can be representing in complex capacitance, C* with the following relationship:

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$$C^* = C' + jC'' \qquad (3)$$

where C' is the real part of capacitance and C" is the imaginary part of capacitance. The real part of capacitance, C' is measure how much energy from an external electric field stored in a material. The imaginary part of capacitance, C" is measure how dissipative or lossy a material is to an external electric field and it is related to the dc conduction of the material. The imaginary part of capacitance, C" is given by:

$$C'' = G/\omega \qquad (4)$$

with G, is the conductance (Ω^{-1}) and ω is a frequency in radian (rad/s). Figure 4 and 5 shows the graph of C' and C" for samples El1, El2 and El3 respectively.

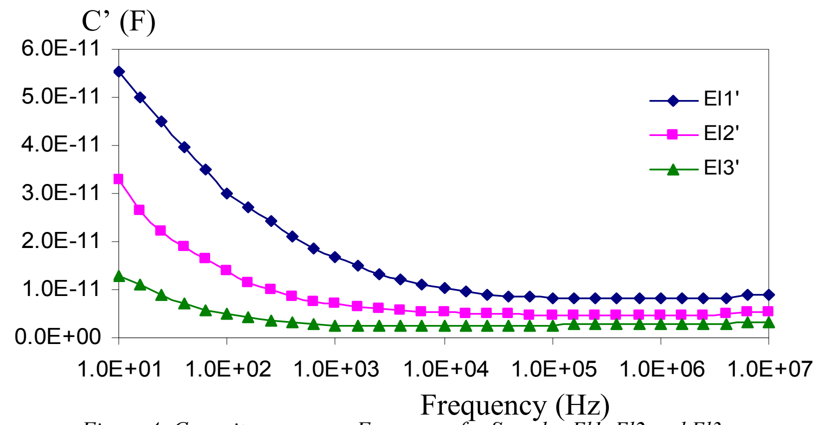

Figure 4: Capacitance versus Frequency for Samples El1, El2 and El3.

Figure 4 shows that all three samples shows decreases in capacitance value with increases of frequency measurement and become constant at the frequency 10 KHz. This decrease in capacitance was observed with increase in frequency because usually at lower frequency the compound exhibit different types of polarization i.e interfacial, dipolar, atomic, atomic [10]. Sample El1 give higher capacitance and value due to the smaller gap compared to the other two samples, contributes to the higher losses in capacitance as shown by Figure 5.

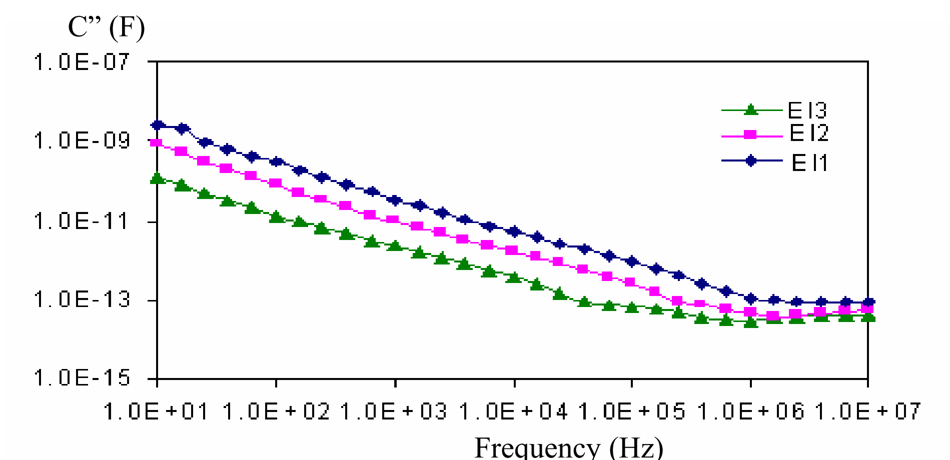

Figure 5: Frequency response of C" for Samples El1, El2 and El3.

From Figure 5, the losses in capacitance, C" for all samples shows a rapid decrease at lower frequency and becomes slow at the higher frequency. The decrease take places when the jumping frequency of electric charge carriers cannot follow the alteration of applied AC electric field beyond a certain critical frequency [10]. It is normal behavior of ceramics. From the capacitance analysis (Figure 4 and 5), it shows that the higher capacitance value give higher losses in capacitance. It show that the different gap of the interdigitated electrode gives a different result in capacitance measurement with the smaller gap gives higher capacitance compared to the bigger gap.

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From the concept of universal law, the experimentally observed behavior for different dielectric dispersion can be explain with dipolar, quasi-dc and diffusive mechanism. Based on this concept, an equivalent circuit is constructed in order to explain the dielectric behavior of the $BaTiO_3$ thick film sample. Figure 6 show the complex capacitance (C',C") plotting with the variation of frequency for the El1 sample. In the same Figure, C' fit and C" fit was plotted for fitting the experiment data based on the equivalent circuit being construct using the concept of universal capacitance as shown by Figure 7. The circuit model consist two element of a quasi-dc mechanism, $C_1\,(\omega)^{-p}$ and $C_2\,(\omega)^{n-1}$ capacitor in parallel. The mathematical expression from the quasi-dc behavior is given by following equation [11]:

$$C_1 = C_1\,(i\omega)^{-p} \qquad \omega << \omega c \qquad (5)$$
$$= C(f_c)\times(\frac{\omega}{\omega_c})^{-p}\left(\cos p\pi/2 - j\sin p\pi/2\right)$$

$$C_2 = C_2\,(i\omega)^{n-1} \qquad \omega >> \omega c \qquad (6)$$
$$= C(f_c)\times(\frac{\omega}{\omega_c})^{n-1}\left(\sin n\pi/2 - j\cos n\pi/2\right)$$

The parameter n is the measure of the degree of correlation within the cluster and parameter p is the perfection of transport of the effective charge displacement by means of the irregular array [10]. The frequency, f_c in this case defines the rate at which charges escape from one cluster and transfer to another via the weakly conducting bonds and ω_c is the frequency rate at which the C' and the C" was intercept.

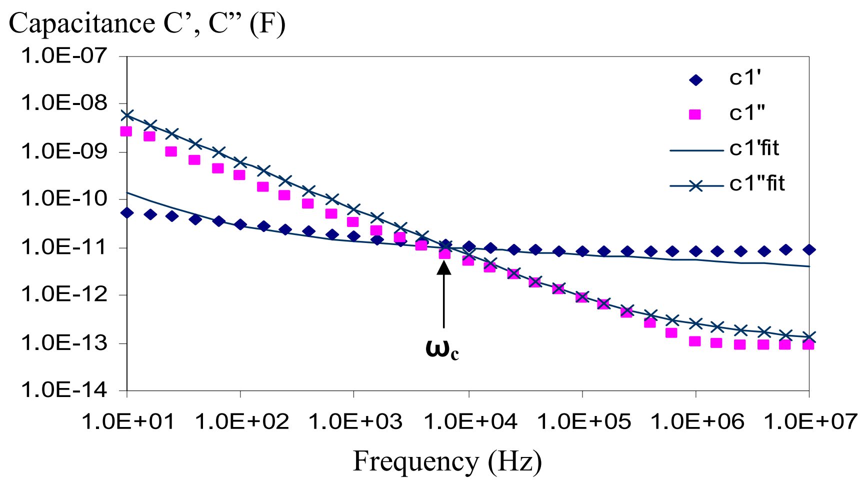

Figure 6: Complex Capacitance versus Frequency for Thick Film Sample

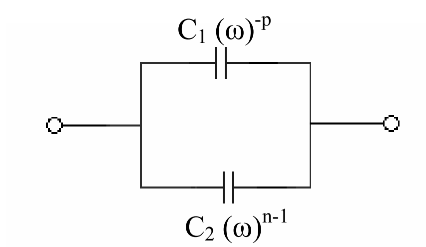

Figure 7: The Circuit Model Represent the Response Mechanism of $BaTiO_3$ Sample.

The value of parameter n and p at the circuit model were determined based on the fitted graph of C'fit and C"fit using the Eq.5 and 6 respectively. The value of p is 0.86 and the value of n is 0.08. It can be observed that the value of p obtained at low frequency close to unity, suggested that the material showed dc conductivity [11]. This mechanism is due to the charge transport between the clusters [10]. The transition frequency f_c, is 3980 Hz

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the capacitance value at the transition frequency, $C(f_c)$ is $1.33\text{x}10^{-11}$ Farad. Both low and high frequency follow the universal response, but with much smaller of the exponent of n observed.

Electrical Resistivity

Electrical resistivity is a measure of how strong a particular material opposes the flow of electric current. A high resistivity is an important characteristic for insulating materials, while low resistivity is an important characteristic for conducting material. The SI unit for electrical resistivity is ohm meter (Ωm). The electrical resistivity, ρ, of dielectric layer on the interdigitated electrode can be defined as

$$\rho = R\frac{A}{l} \tag{7}$$

where ρ is electrical resistivity, *R* is a resistance of the test material, *A* is total area of opposed electrode, and *l* is gap between two electrode [1]. The area (*A*) and the length gap (*l*) of electrode in each samples were determined from the design mesh, while the resistance (*R*) value was determined from IV curve measured using Keithly 4200-SCS. Figure 8 shows the current versus voltage (IV curve) for sample El1, El2 and El3.

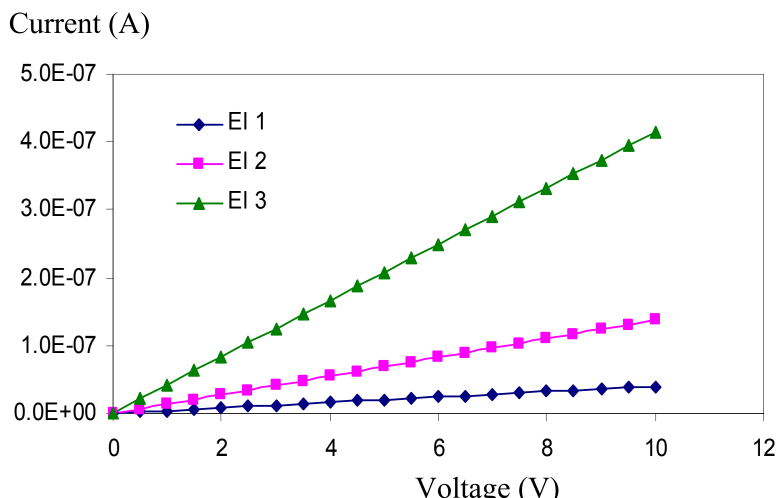

Figure 8: Current versus Voltage for Sample El1, El2 and El3

The IV curve for all samples showed a good linearity between current and voltage ranging from 0 to 10 volt. Using the Eq.7, the electrical resistivity, ρ and material resistance, R for each sample were calculated and listed in Table 3.

Table 3: Resistance and electrical resistivity value of thick film samples

Samples	R(Ω)	ρ(Ωm)
El 1	$24.1\text{x}10^6$	$15.0\text{x}10^3$
El 2	$72.9\text{x}10^6$	$30.4\text{x}10^3$
El 3	$250\text{x}10^6$	$78.1\text{x}10^3$

From Table 3, the El 3 sample shows the highest resistance and highest electrical resistivity followed by samples El2 and El1. The highest resistance value was observed in sample El 3 due to the biggest gap between two conducting electrode. Generally, the resistance of the test material is proportional to the length gap of interdigitated electrode as given by Eq.7. As the gap between two conductor increases, the resistance will increase and this is justify with the result obtain as shown by Figure 8.

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CONCLUSION

In this works, the reliable pastes for dielectric material were successful prepared by mixing the $BaTiO_3$ powder to organic vehicle in ratio of 70:30. The organic vehicles were form by terpineol solvent and ethyl cellulose resins in ratio of 12:1. The pastes were screen printed on the ceramic substrate have show a good printing quality and has been characterized based on different gap of interdigitated electrode pattern. The measurement results show that the smaller gap between intedigitated electrodes gives higher capacitance value and higher dielectric losses compared to the bigger gap. Based on quasi-dc mechanism, the equivalent circuit for the $BaTiO_3$ thick film was constructed to represent the dielectric behavior of the film with electric field. The dc resistivity of the material gives ohmic response with the bigger gap of interdigitated electrode show a higher resistance compared to the smaller gap. As a conclusion, the electrical properties of $BaTiO_3$ layer are affected by the gap of the intedigitated electrode pattern and the design electrode parameter should be optimize when sensitivity issue are important such in thick film sensor fabrication.

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