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RESEARCH ARTICLE

Preparation of Metal-Thin Film-Metal Device Structure for Pyroelectric Heat Sensor Measurement

Pyroelektrik Isı Sensörü Ölçümü İçin Metal-İnce Film-Metal Cihaz Yapısının Hazırlanması

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ABSTRACT: In this study, the pyroelectric properties of organic Langmuir-Blodgett (LB) thin film material produced at the nanometer scale were investigated. LB thin films obtained by transferring organic molecules floating on the water surface to the solid surface were produced in an unsymmetrical structure. Steric acid and eicosylamine molecules were selected to fabricate unsymmetrical LB film structure. This structure was used to investigate the pyroelectric and electrical (C-f and C-tan δ) measurements. The pyroelectric figure of merit (FOM) was determined using pyroelectric constant, the dielectric constant value and dielectric loss. The value of FOM for the stearic acid/eicosylamine LB film was determined as 0.530 $\mu Cm^{-2}K^{-1}$.

Keywords: Pyroelectric effect, Langmuir-Blodgett thin film, electrical measurements, stearic acid, eicosylamine

ÖZ: Bu çalışmada, nanometre ölçeğinde üretilen organik Langmuir-Blodgett (LB) ince film malzemesinin piroelektrik özellikleri incelenmiştir. Su yüzeyinde yüzen organik moleküllerin katı yüzeye aktarılmasıyla elde edilen LB ince filmler simetrik olmayan bir yapıda üretilmiştir. Simetrik olmayan LB film yapısını imal etmek için sterik asit ve eikosilamin molekülleri seçildi. Bu yapı, piroelektrik ve elektriksel (C-f ve C-tan δ) ölçümlerini araştırmak için kullanıldı. Piroelektrik figüre of merit (FOM) değeri piroelektrik sabiti, dielektrik sabiti değeri ve dielektrik kaybı kullanılarak hesaplandı. Sterik asit/eikosilamin LB filmi için FOM değeri 0.530 $\mu Cm^{-2}K^{-1}$ olarak elde edilmiştir.

Anahtar Kelimeler: Piroelektrik etki, Langmuir-Blodgett ince filmi, elektriksel ölçümler, sterik asit, eikosilamin

1. INTRODUCTION

The pyroelectric effect is electrical polarization due to temperature change [1]. The best examples of pyroelectric single crystals are barium titanium oxide ($BaTiO_3$) [2] and triglycerinsulfate (TGS) [3]. $BaTiO_3$ and TGS materials are used in thermal imaging devices. These materials show a high pyroelectric activity. The disadvantages of these materials are to have a high dielectric constant and high dielectric losses. Unfortunately, the easily fragile structure of TGS is an important disadvantage. In addition, it is very difficult to process and change its structure due to its solubility in water. Other examples of single crystals such as lithium tantalate ($LiTaO_3$), strontium barium niobate ($Sr_{1-x}Ba_xNb_2O_6$) and lithium niobate ($LiNbO_3$) are known to undergo structural degradation at high temperatures, however these materials are promising for thermal imaging applications due to their durable structure [4].

Ceramic pyroelectric materials can be prepared easily and at low cost compared to single crystals. Ceramics, which are in the class of high-performance pyroelectric materials, have a durable structure. An example of the most well-known is

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the lead zirconate titanate (PZT) [5]. Ceramics can be produced in various thicknesses up to 10 µm. Ferroelectric polymers such as polyvinylidenefluoride (PVDF) show strong piezoelectric and pyroelectric properties. Polymers behave similarly to the behaviour of monomers and are formed by dissolving them in a suitable solvent, as in monomeric substances [6].

Organic Langmuir-Blodgett (LB) film materials are alternative materials for the thermal imaging devices such as pyroelectric heat sensor application due to a cost-effective compared to ceramics and single crystals. Due to the highly ordered structure of LB films, pyroelectric detectors have been extensively studied [7-12]. The unsymmetrical LB film material produces a current when heated or cooled. This phenomenon is called the pyroelectric effect. In addition, LB film materials have low dielectric constant and dielectric losses. However, the pyroelectric coefficients of LB film materials are lower than the pyroelectric coefficients of other pyroelectric materials [13].

LB film technique is a suitable technique to produce symmetrical or unsymmetrical organic thin films at the water surface. The thickness of the produced LB films can be controlled at the nanometer level (the thickness of a single molecule) [14-16]. The chemical structure of steric acid and eicosylamine molecules are given in Figure 1. Steric acid material is one of the well-known LB film material which contains a water-loving carboxylic acid group ($-CO_2H$) at one end and a water hating long hydrocarbon group ($C_{17}H_{35}-$) at the other end. Eicosylamine has a similar structure to the stearic acid molecule, instead of the water-loving carboxylic acid group, the amine group (NH_2) group. The novelty of this work is to use these two materials for a non-centrosymmetric LB film as a heat-sensor device and to obtain the Figure of Merit (FOM) value which is important parameter choosing heat-sensor devices.

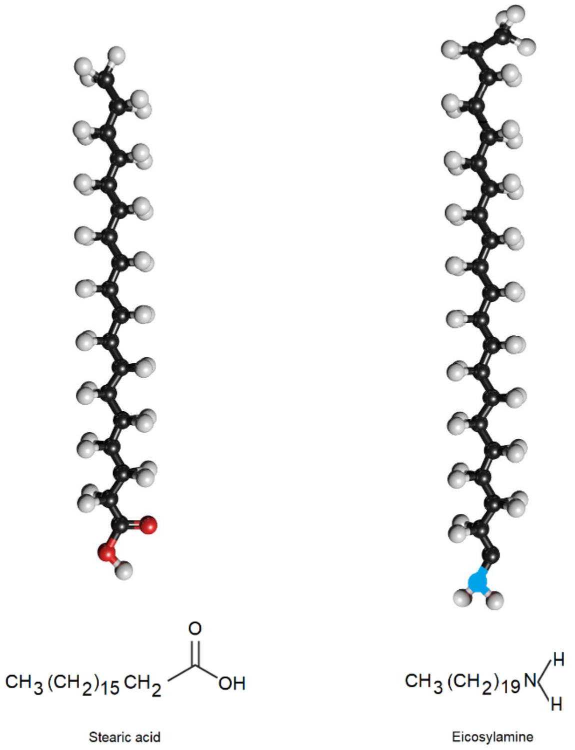


Figure 1: Chemical structure of materials.

In this paper, the LB thin film materials such as steric acid and eicosylamine are prepared to contain an unsymmetrical structure with one layer of acid and the other layer of amine. During LB film fabrication, LB film was followed step by step to monitor the transfer rate and surface area change which are important parameters in determining the film quality. The pyroelectric measurement and the variation of frequency according to capacitance and dielectric losses changes are detailed. FOM value for pyro device is determined using these experimental measurements.

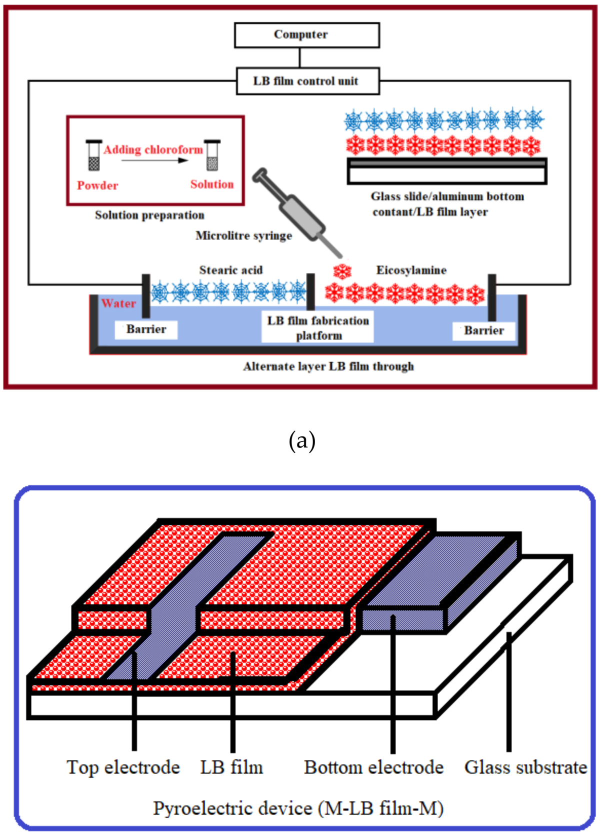
2. EXPERIMENTAL DETAILS

2.1 Device Fabrication Process

Super premium microscope glass slides were used for LB film coating. They were placed in a specially prepared and compartmentalized glass box, 10% decontaminated soap (decon 90) and 90% distilled water were added into a beaker. The beaker was placed in an ultrasonic bath and mixed for 15 minutes. The rinsing process is with 100% pure water and is repeated five times in an ultrasonic mixer for 15 minutes each. With the completion of the cleaning process, the next step, the aluminum coating process, was started on the glass slides. For the preparation of the bottom aluminum contact, the glass slide was placed in the specially prepared mask and were placed inside the Edwards Coating System E306 evaporator system. The E306 evaporator system was put into vacuum for 24 hours. After providing the appropriate vacuum conditions, the aluminum evaporation process was started. Evaporation was done slowly at a rate of 0.1-0.3 Å/s up to 50 Å and 1-3 Å/s is reached and up to 500 Å. After than the system automatically was shut down and was waits for at least one hour to cool.

The LB thin film technique Is well known method to fabricate ultra-thin film devices for sensor applications which can be use in the field of nanotechnology. The basic fabrication process is to produce LB films from a floating monolayer to a solid substrate which can be moved from up to down. The biggest advantages of LB film technique is that the molecular arrangement of the film can be controlled during thin film production. NIMA 622 model alternate layer LB through was employed to fabricate a non-centrosymmetric stearic acid/eicosylamine LB film device. When the fabrication of bottom electrode was completed onto the glass slide, it is ready to prepare for the LB film fabrication process. There are certain conditions for film production (see Figure 2a) to occur by transferring molecules from the water surface to a solid surface.

LB film material was spread on the water surface with the help of a micro syringe, and then the solvent in it was evaporated. The barriers were gradually compressed to the solid phase state. Following this process, LB film production started. By moving the platform where the solid surface was located in water-thin layer-air-thin layer-water environments, LB film production was transferred to the solid surface (glass+Al_2O_3) in thin layers. By repeating this process, as much thin layer as desired was transferred to the solid surface. LB film fabrication process is made at the room temperature.



(a)

(b)

Figure 2: a) Fabrication process of LB film structure b) Metal/LB film/Metal device structure.

LB films produced by this method were alternate layer type LB film. After the LB film fabrication process, it was passed to the upper contact coating following the LB film coating process. Top contact coating is required to obtain Metal/LB film/metal (M-LB-M) structure of LB film layers transferred onto glass+Al_2O_3. 50 nm thick top contact was prepared using the same evaporation procedure used for 50 nm thick bottom contact. The shape of the top contact coating used to create the final device structure is shown in Figure 2b.

2.2 *Measurement Process*

All electrical measurements were made with the help of aluminum coated lower and upper electrodes. To ensure good contact between the electrodes, a material named RS 186-3593 Silver Conductive Paint was used. After these steps, the produced LB film device contact connections were made and placed in the electrical measurement system given in Figure 3.

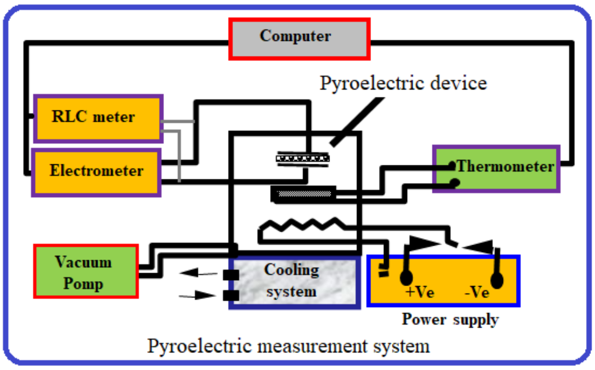


Figure 3: Schematic diagram of electrical measurement system.

The pyroelectric effect is briefly defined as electrical polarization due to temperature change. For example, when a material is heated or cooled, a temperature gradient forms on the material and this material produces a current. This current is called pyroelectric current and the phenomenon is called pyroelectric effect. In the pyroelectric effect, the electrical polarization of the substance changes with the temperature gradient. Pyroelectric measurements were taken by applying a temperature gradient onto LB film device. Dielectric measurements were taken from 100 Hz to 1 MHz.

2.3 *Results and discussion*

The pyroelectric current produced by the LB film is given in Equation 1 as:

$$I = \Gamma A \frac{dT}{dt} \qquad (1)$$

where Γ is the pyroelectric coefficient, A is the measurement area and dT/dt is the rate of temperature change. It can be seen from Equation 1, if the temperature does not change with time, no pyroelectric current is observed. The pyroelectric coefficient is used as an important parameter in the comparison of heat sensor materials and in understanding their electrical polarization behaviour.

A quasi-static pyroelectric measurement technique can be used to investigate pyroelectric properties of thin films. These films is heated and cooled by a non-radiative source with a small temperature change (usually ± 1K) controlled by a Peltier heater. Figure 4 shows an ideal form of a quasi-static pyroelectric measurement (Temperature and pyroelectric current changes as a function of time).

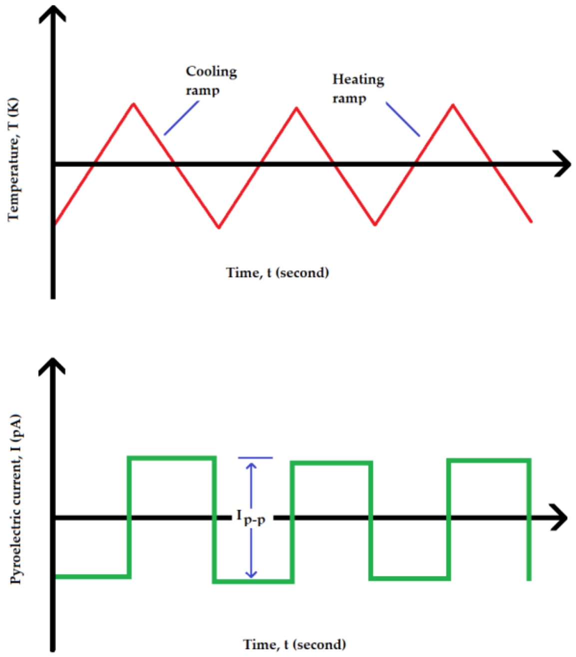


Figure 4: An ideal form of a triangular temperature profile for a square-wave pyroelectric current change.

If the electrode area of thin film sample is constant, the temperature gradient can be applied to the thin film by slowly heating or cooling of the sample. As a result of heating $(dT/dt)_{heating}$ or cooling $(dT/dt)_{cooling}$ ramp (with red colour), the sample yields a pyroelectric current (I_{p-p}) (with green colour) given in Figure 4. The total rate of temperature change can be measured from the triangular temperature profile and can be described as:

$$\left(\frac{dT}{dt}\right)_{Total} = \left|\left(\frac{dT}{dt}\right)_{heating}\right| + \left|\left(\frac{dT}{dt}\right)_{cooling}\right| \qquad (2)$$

From Equation 1, it can be seen that a linear relationship between I_{p-p} and $\left(\frac{dT}{dt}\right)_{Total}$ should be expected.

The LB film device for pyroelectric heat sensor applications is required that it should produce the highest pyroelectric current. In addition, organic LB films are an alternative material against single crystal, ceramic and other pyro materials due to easy fabrication process, low cost, highly ordered preparation and easy control of molecular structure.

Pyroelectric results of temperature ramps and pyroelectric current for stearic acid/eicosylamine LB film is given in Figure 5. When the temperature gradient (red colour) is slowly increased, LB film produced a pyroelectric current (green colour) due to a new molecular arrangement of stearic acid/eicosylamine LB film structure depends on temperature changes. These graphs were used to determine Γ of stearic acid/eicosylamine LB film used for the FOM value. The value of Γ for the stearic acid/eicosylamine LB film material produced within the scope of this study was calculated as 0.587 $\mu Cm^{-2}K^{-1}$.

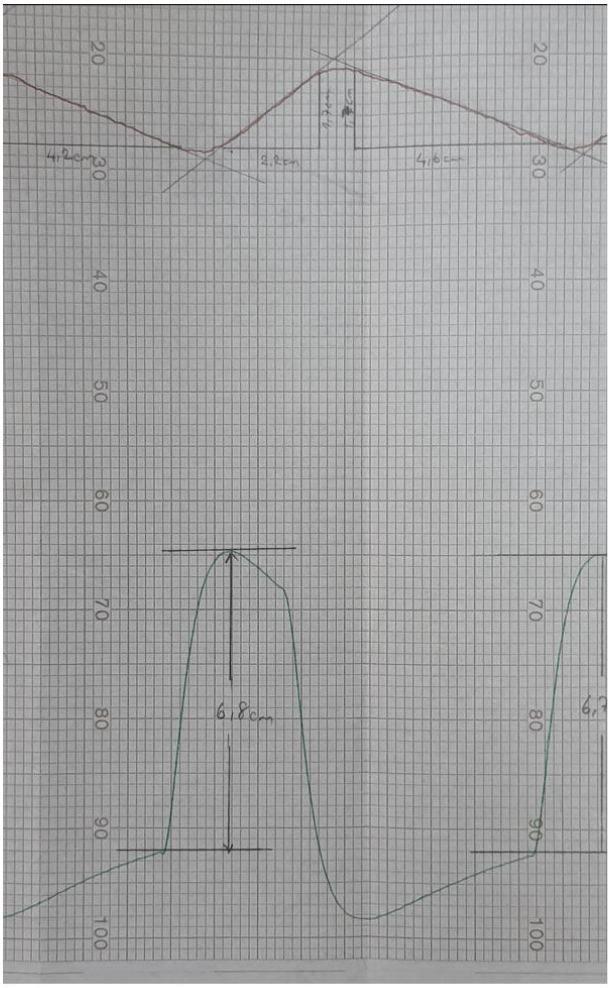


Figure 5: An experimental measurement between a triangular temperature profile and a square-wave pyroelectric current change.

FOM described at Equation 3 is an important parameter to design of pyroelectric thermal imaging devices.

$$FOM = \frac{\Gamma}{\sqrt{\varepsilon tan\delta}} \tag{3}$$

where ε is the dielectric constant and tan δ is the dielectric loss. To find out dielectric properties of our device, capacitance and dielectric loss measurements were taken as a function of frequency.

Experimental results were presented for dielectric relaxation in our M-LB-M pyro device along with the evaluation of values of relevant physical parameters. Figure 6 gives dielectric measurements of stearic acid/eicosylamine LB film. The variation in AC capacitance and tan δ versus the frequency (log f). Capacitance result shows small decrease initially and then a sharp reduction with increasing frequency. The behaviour pattern for tan δ is, on the other hand, opposite.

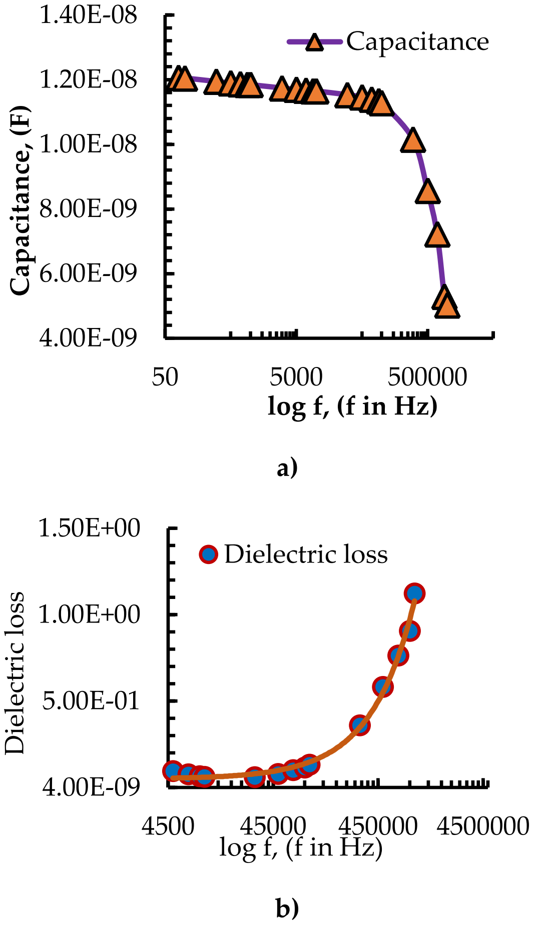
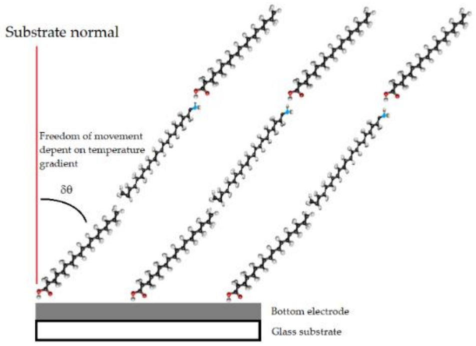


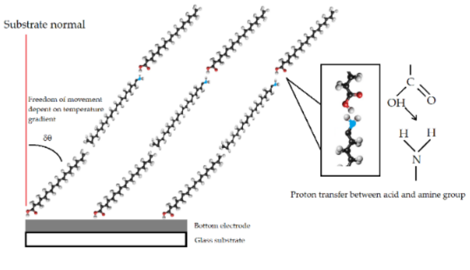
Figure 6: AC measurements of a) capacitance, b) dielectric loss (tan δ) as a function of frequency.

The capacitance and dielectric losses as a function of the logarithmic frequency can be used to investigate the dielectric behaviour of LB film. These graphs are very useful to determine ε and tan δ values which can be used for the calculation of FOM value. Using Figures 5, 6 and Equation 3, FOM value of our LB film structure is calculated to be 0.530 $\mu Cm^{-2}K^{-1}$.

According to the literature there are three main components of the pyroelectric contribution in LB films. These are known as tilting [17] [18], proton transfer [19] [20] and ionic mechanism [21-23] respectively. In our case tilting and proton transfer mechanisms are occurred and they are shown symbolically in Figure 7. Tilting mechanism is based on the principle that thin layers are tilted at a certain angle because of temperature change. Proton transfer, on the other hand, is based on proton exchange between $-COO^-$ (in the structure of stearic acid) and $-NH_2^+$ (in the structure of eicosylamine) groups. This interaction between acid and amine groups which depends on temperature change. In both mechanisms, electrical polarization due to temperature change is observed, and LB films produce a pyroelectric current.



a)



b)

Figure 7: Pyroelectric interaction mechanisms a) tilting b) proton transfer

The ionic mechanism in the substances used in this study does not play a role because of no free ions between stearic acid and eicosylamine LB film structure. It can be concluded that the pyroelectric effect here is entirely dependent on tilting and proton transfer.

Author Contributions:
Rifat Çapan: Experimental & Measurements, Investigation¸ Writing, Review & Editing.
Zikriye Özbek: Investigation¸ Writing, Review & Editing.

Conflicts of Interest:
The authors report no conflicts of interest.

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