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ACENTRIC LANGMUIR-BLODGETT FILM ASSEMBLIES

BY

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Never say anything remarkable.
It is sure to be wrong.

Mark Rutherford (1915)

DECLARATION

I hereby declare that the work carried out in this thesis has not previously been submitted for any degree and is not being currently submitted in canditature for any other degree.

Signed Phillip Christie

The work carried out in this thesis was carried out by the candidate.

Signed McPetty

Gareth Roberts

Directors of Studies

Phillip Christie

Candidate

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ABSTRACT

In recent years there has been considerable interest in the use of Langmuir-Blodgett (LB) films as the basis of active and passive thin film devices. One such appliction is in room temperature, pyroelectric thermal imaging systems. As the detectivity of these sensors is approximately inversely proportional to thickness, there may be significant advantage in exploiting the ability of the LB process to produce ultra-thin layers.

Here we report the use of the LB technique to fabricate molecular assemblies with precisely defined symmetry properties. This has made possible the construction of ultra-thin organic films possessing the spontaneous polarisation necessary for the observation of the pyroelectric effect. Two distinct approaches are adopted to produce the required molecular packing arrangements. The first uses the ability of a novel alternate layer trough to assemble acentric ABAB structures. Various materials are studied for their suitability for alternate layer deposition. The co-deposition of fatty acids and amines produces alternate layer assemblies with a high degree of structural and electrical integrity. The second approach uses a novel polymeric LB film. Polybutadiene (PBD) is observed to deposit in highly asymmetric X-type layers if the transferred monolayer is exposed to u.v. radiation between each deposition step.

The structural and electrical properties are characterised. The presence of the unique polar axis associated with pyroelectric materials is investigated using surface potential measurements. Dynamic and quasi-static detection techniques are employed to detect the pyroelectric activity within the assemblies. For the first time pyroelectric activity is observed in "thin" (11 layer) acid/amine assemblies. The pyroelectric coefficient is found to be thickness dependent, increasing for larger numbers of layers; the coefficient for a 99 layer sample is comparable to that of PVDF, a commercially available pyroelectric polymer.

The incorporation of LB films into thin PVDF Metal Insulator Metal (MIM) structures is also investigated. The presence of a stable phthalocyanine LB film is shown to increase the electrical breakdown strength of the device. Finally the incorporation of highly polarisable sulphur substitutions into fatty acid LB films is reported. The permittivity is found to increase in proportion to the number of sulphur atoms introduced into the hydrocarbon chain.

CONTENTS

CHAPTER 5 - DEVICE FABRICATION AND EXPERIMENTAL TECHNIQUES

CHAPTER 6 - ALTERNATE LAYER LB FILM ASSEMBLIES : RESULTS AND DISCUSSION

CHAPTER 1

INTRODUCTION

One of the most active areas in solid state research today is the study of pyroelectricity, both as a means for investigating fundamental physics and as a phenomenon useful in infra-red detectors. Since the realisation of the many technological applications of the pyroelectric effect, the publication rate has been doubling every three years (see figure 1.1).

All crystalline materials may be classified according to the symmetry of their unit cell(1). Unit cells with no centre of symmetry are said to be acentric and they have the property that a polarisation may be induced by an applied mechanical stress. Some of these acentric classes also possess the important property that a finite and permanent polarisation exists in the absence of an applied field or stress. If this spontaneous polarisation can be varied by heating or cooling a current will result in an external circuit, which is proportional to the rate of change of temperature. This phenomenon is called pyroelectricity and it has received much attention since Hadni(2) suggested the pyroelectric vidicon for thermal imaging in 1965. The interest in pyroelectric imaging systems stems from its ability to suppress high levels of background radiation and sense only temperature differences, without the complex scan mechanisms and cooling systems required by other imaging technologies(3). Currently the performance of pyroelectric imaging systems is limited by noise in the detector material. This has led to a move towards thin film technology since it can be shown(4) that the high frequency noise equivalent power of the detector is proportional to thickness.

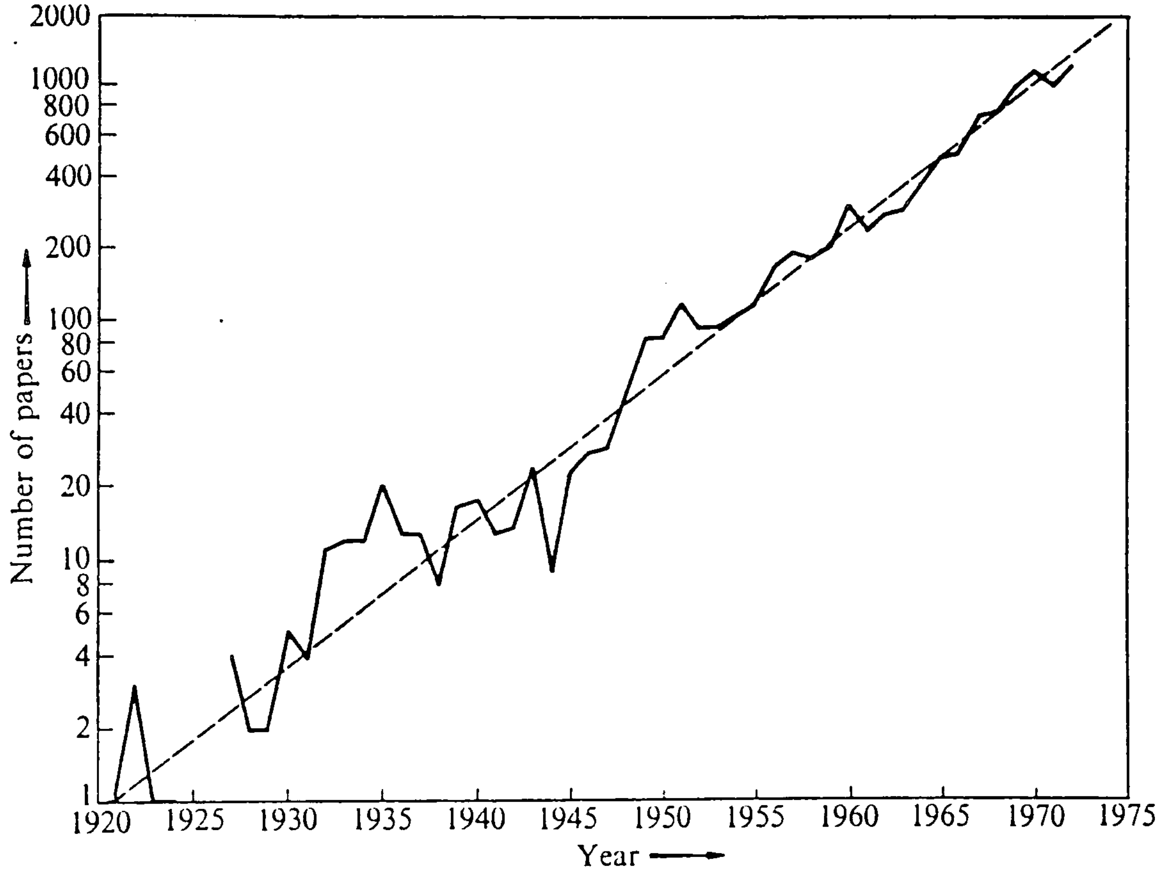

Figure 1.1 Number of publications on pyroelectricity and related topics as a function of year (After Landolt-Bornstein New Series, Group III, Vol-9, Springer-Verlag, Berlin (1975))

In this thesis the Langmuir-Blodgett technique has been used to fabricate crystal structures with precisely defined symmetry properties. This control over the molecular architecture of organic crystals is unique to the LB technique and has enabled the construction of ultra-thin organic films possessing no centre of symmetry and with the spontaneous polarisation necessary for the observation of the pyroelectric effect.

The strange properties of pyroelectric materials have been observed since ancient times because of the ability of certain minerals to attract small objects when they are heated. Thus chapter 2 describes the historical development of the effect and includes a phenomenological model based on purely thermodynamic arguments. The properties of acentric crystals are then discussed on a molecular level and the arguments extended to organic systems. Chapter 3 briefly covers the dielectric characterisation of LB film materials and surveys the polarisation mechanisms responsible for the frequency response of dielectric materials. LB film technology is introduced in chapter 4; this includes the historical background, experimental procedures and an outline of possible applications of the technique. In chapter 5 the various experimental arrangements used during the course of this study are described and the techniques of device fabrication are listed. Also included are the results of novel investigations into increasing the emissivity of LB film infra-red detectors. Chapters 6 and 7 contain the bulk of the experimental data. The first of these deals with the production of alternate layer structures for the observation of the pyroelectric effect whilst the second describes the results for the X-type deposition of a novel polymeric LB film. In chapter 8 a summary of related work is discussed. The closing chapter of this thesis reviews the conclusions and gives suggestions for further work.

CHAPTER 2

PROPERTIES OF ACENTRIC STRUCTURES

2.0 INTRODUCTION

This chapter is concerned with the properties of polar molecular crystals which possess no centre of symmetry; so called polar acentric structures. If these acentric structures also possess a unique polar axis, then a spontaneous polarisation may exist across the crystal. This spontaneous polarisation produces extremely large electric fields within the sample and consequently the dielectric properties of such structures would be expected to differ from their centrosymmetric counterparts.

If the polarisation may be varied by an applied stress then the material is termed piezoelectric, from the Greek verb πιεζειν, to press. Similarly if the polarisation existing across the sample may be varied by heating then the material is termed pyroelectric (from the Greek πγνροζ = fire). The two effects are closely inter-related and section 2.2 attempts to illustrate the relationships between the polarisation of a crystal and its associated piezo- and pyroelectric effects using a simple thermodynamic model. Section 2.3 describes, on a microscopic level, the importance of crystal symmetry in the production of a large spontaneous polarisation.

Finally, section 2.4 shows how inhomogeneous systems may produce effects which closely resemble the properties of acentric crystal structures.

The next section gives a brief outline of the history and applications of this technologically important class of materials.

2.1 AN HISTORICAL OUTLINE

The strange properties of acentric structures have been known since ancient times because of the ability of certain materials to attract objects when they are heated. Possibly the earliest description of the large polarisation associated with such materials, was by Theophrastus, the Greek philosopher, in a passage written 23 centuries ago:

> '... remarkable in its powers, and so is the lyngourion, for seals are cut from this too, and it is very hard, like real stone. It has the power of attraction, just as amber has, and some say that it not only attracts straws and bits of wood, but also copper and iron, if the pieces are thin, as Diokles used to explain.'
>
> Theophrastus C.315 B.C.

Theophrastus was a pupil of Aristotle and the above extract was from a treatise on minerals(1). For 1800 years it was a most valuable and authoritative work on mineralogy. The lyngourion stone mentioned was highly prized for its curative powers and was probably the precious stone tourmaline.

Two thousand years after Theophrastus, the strange properties of tourmaline were re-introduced into Europe, through the publication, in 1707, of a book entitled 'Curiose Speculationes bey Schlafosen Nachten' (Curious speculations during sleepless nights). Here the author, Johan Schmidt, wrote of the curious property of trip or tourmaline, to attract ashes from burning coals and then repel them.

> '... This sight was very amusing for as soon as a small quantity of ashes leaped upon it, they appeared to be endeavouring to writhe themselves by force into the stone. Soon a few of the ashes jumped from it again, as if to leap to the tourmaline again.'

It was also in the 18th century that true scientific experimentation