Introduction

It was during my early years in robotics research, looking at pyrometers for use in rapid tactile sensing that I came across Langmuir-Blodgett films (LB-films). There was much interest in those days in extending tactile sensing to more than just force and displacement measurements and thermal properties was one such additional parameter to be investigated. Most thermal tactile sensor designs at this time relied on the smallest available thermistor and some form of heat source. Needless to say such configurations had rise times of several seconds which was not considered fast enough for modern automation tasks. The next step was to try infra-red techniques. Although ferroelectric pyrometers can be an order of magnitude faster than similarly sized thermistors, their thermal time constants are noticeably longer than their respective electrical time constants. For tactile sensing purposes, sensitivity was a less important issue and we had successfully built and tested a number of pyrometer based designs with response times down to a few hundred milliseconds (Monkman and Taylor, 1993), but we were not altogether satisfied and still sought something faster.

Once the province of chemistry departments, LB-films is one of those areas of research somewhere between chemistry, physics and engineering which is often turning up something new despite the major complaint from detractors that nothing has yet reached the marketplace. The use of LB-films as pyrometers is now established technology, however, as they are still somewhat obscure it is worth taking some time to explain what they are.

Most children are fascinated by the way an oil film floating on the surface of a puddle appears to reflect light in rainbow colours. Of course the reason lies in the fact that the molecules of oil align themselves to form what is effectively a diffraction grating. Motor oil is a comparatively simple molecule with a large degree of symmetry, but what happens if we place a few drops of another substance whose molecular structure is chemically asymmetrical? Stearic acid, whose molecular chain consists of a fatty (carboxylic) acid end (COOH) and a hydrocarbon (alkyl) chain (C_nH_{2n+1}), is one particularly good example of a suitable surface active material. When stearic acid comes into contact with water, the acid...
end of the molecular chain tries to dissolve itself in the water but the hydrocarbon end prevents it from doing so because the chain will not easily break. Consequently the molecules immediately align themselves with one end in contact with the water while the other end floats above the surface. The end result is a relatively well orientated monomolecular layer floating on the water’s surface. Well, that is effectively what Irving Langmuir and Katherine Burr Blodgett discovered whilst working in the General Electric research labs during the 1930s. Today the phenomenon is enjoying renewed interest as such monomolecular layers have some very interesting properties and in many cases they can be made sensitive to particular biological or chemical compounds.

The manufacture of an LB-film is relatively straightforward. A measured quantity of a compound whose molecular structure exhibits a hydrophobic end and a hydrophilic end is placed on the surface of a trough of water. The molecules immediately start to spread out as shown in Figure 1(a). A little force is then applied to compress the molecules together to form a compact monomolecular layer as depicted in Figure 1(b). In more advanced systems, precise film tension measurements are made to ensure that the film is complete and as free from defects as possible. If a solid substrate is now dipped into the middle of this film at a well controlled constant rate, the hydrophobic surface of the molecular film will tend to adhere to the substrate surface as illustrated in Figure 1(c).

If desired, multiple monolayer films can be built up by repeating the dipping process as shown in Figure 1(d). In practice it is often difficult to maintain a constant surface tension during the dipping process and inhomogeneities in the final film can reduce its effectiveness. Nevertheless, up to 100 or so molecular layers can be built up over one another in this way.

Organic compounds like phthalocyanine and porphyrins are often used in electrically conductive LB-film materials where additional charge carriers can be generated as a result of interaction with aggressive gases like ammonia or nitrogen dioxide.

The design shown in Figure 2(a) is relatively simple. A pair of interdigital

![Figure 1: Langmuir-Blodgett film production](image-url)
electrodes are formed on an insulating substrate and an LB-film is laid over the surface. The electrical resistance of the sensor changes as molecules, to which the LB-film is sensitive, come into contact with the film’s surface.

Most conventional gas sensors suffer from problems of long-term stability and LB-film based gas sensors are inclined to degrade even more quickly. In many cases the LB-Film structure can be stabilised by cross-linking. Partial cross-linking of selected areas can also be achieved using photochemical ultra-violet light irradiation. The uncross-linked parts may then be chemically removed. Diffusion barriers for chemical sensors have been created in this way (Salamon, 1996).

In the case of LB-film bio-sensors, there exists a number of suitable naturally occurring organic polymers like chlorophyll and cholesterol. If an antigen is bound to such an LB-film membrane and a free antibody is specifically adsorbed by its surface, the electrical potential across the membrane will change. However, the response time can be rather long, as may be seen from Figure 2(b), and selectivity is often poor. In cases where the organic LB-film materials used have completely saturated chemical bonds few charge carriers are available to produce any current flow. Consequently, LB-film based sensors tend to be capacitive, relying on dielectric polarisation as a result of some external stimulus (Petty, 1996). Other designs rely on measuring changes in mechanical properties as a result of interaction between the LB-film and biochemical species. Examples include surface acoustic wave or quartz microbalance technology as discussed in a previous issue of this journal (Monkman, 1996).

The technique of infra-red spectroscopy is based on the fact that most molecules have distinct bands of absorption within the infra-red spectrum giving rise to almost unique characteristics for most polymers. In some cases the wavelength susceptibility extends well into the visible and even ultra-violet spectra. This energy absorption usually results from the molecules in question being sent into vibrational states. A large polymer chain consisting of many different chemical structures along its length can be analysed step by step as the frequency of the impinging infra-red radiation is changed and the resulting absorption measured. Each different part of the chain has a different molecular structure which corresponds to a particular frequency, or narrow band, of vibration. An LB-film is of course a planar surface having homogeneous molecular structure. When irradiated, the complete surface will react in unison.

The ability of many chemicals to re-emit light (fluorescence) at a frequency different from that with which it is irradiated is well-known and it is this phenomenon, when coupled with the advantages offered by LB-films, which offers many attractive possibilities for an interface between the biochemical world and opto-electronics.

Compounds possessing isoalloxazine rings, and in particular riboflavin, are ideal because they can be chemically and electrically switched between oxidised and reduced states (Patel and Phadke, 1995). However, what is of greatest interest to many are the fluorescence properties.

Figure 3 shows the fluorescence peaks at 528nm and 630nm from a multi-layer LB-film formed from a mixture of stearic acid and
riboflavin excited at a wavelength of 450nm. Although riboflavin in aqueous solution alone exhibits the 528nm fluorescence peak shown in Figure 3, the 630nm peak is only observable when the riboflavin is deposited as an LB-film.

Provided with enough energy, certain dyes can be made to resonate and emit coherent radiation, usually at a wavelength somewhat longer than that of the pumping energy source. Naturally, the attaching of such dye molecules to the polymer structure of LB-films has stimulated many new ideas, though nothing has yet emerged in the form of an LB-film dye laser.

A related, and perhaps more immediately usable, optical effect is that of second (and higher) harmonic generation due to non-linear photoinduced electric dipole polarisation. Special pigments can be stimulated at a particular optical frequency causing it to re-emit radiation at its second harmonic-frequency doubling. By forming LB-films from a fatty acid (typically stearic, arachic or behenic) and an appropriate polymethine or spiran dye, a relatively large surface area can be illuminated to achieve second harmonic generation (Chudinova et al., 1998). Figure 4 shows the efficiency of second harmonic generation for differing number of LB-film monolayers.

Large molecules come quite literally in many different shapes and sizes, though the basic molecular structure remains the same. These differing molecular configurations are called isomers. LB-films are usually too compact for large physical changes in molecular orientation and alignment to take place, but the shape of the polymer may be altered (to another isomeric form) by external stimuli.

Consequently, LB-films which are susceptible to particular biological or chemical species undergo changes in surface topology as a result of such interactions. This in turn results in changes in the state of polarisation of the reflected light which can be detected and measured in comparison to the degree of polarisation of the original illumination – optical ellipsometry. Furthermore, such isomeric changes can be induced optically when certain LB-film configurations are irradiated by polarised light. This is expected to have particular bearing on the future potential for re-writeable mass data storage (Menzel et al., 1998).

Given that the basic optical principle behind the liquid crystal display is the controlled rotation of optical polarisation, then it should come as no surprise that the incorporation of liquid crystal compounds into LB-films is also of considerable interest. Returning to the subject of infra-red pyrometry; it is exactly this area of research being intensively studied at the Physics department of the Ivanovo State University in Russia where increased sensitivity to infra-red radiation through the binding of liquid crystal chiral monomers to LB-film polymers has been successfully achieved (Alexandrov et al., 1999). With such a wide range of possibilities we should expect to see something new on the market soon – hopefully before the next millennium.

References


