Extended Abstracts of the 15th Conference on Solid State Devices and Materials, Tokyo, 1983, pp. 181-184

B-4-1

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Organic Monomolecular Films and Their Applications

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A review is given for Langmuir-Blodgett (LB) films — assemblies of monomolecular sheets (monolayers) stacked one on top of another —as ultrathin films of potential use in electronics. The recent advances in the investigation are outlined together with the historical background. It is shown that a great progress has actually been made in the last several years. A number of molecular species are now available for construction of supermolecular structures. Polymerizable LB films have been developed to ensure the thermal and mechanical strength. Feasibility of some devices have been demonstrated utilizing LB films.

§1. Introduction

The earliest technical application of organic monomolecular layer is, according to H. Kuhn[1], a Japanese dyer's art "sumi-nagashi", where sumi is Chinese black ink made of lampblack and gelatinous protein such as glue, and nagashi means to let flow[2]. This art was established already in the 10th century.

The liquid sumi, a suspension of submicron carbon particles and protein molecules, is spread on the surface of water as a dark thin film. Application of gelatine, soap or greasy matter changes the sumi film into a patchwork of dark and colorless domains. Disturbance of water results in the characteristic pattern, sometimes compared to a well-finished surface of marble, which is transferred by applying a sheet of paper upon the water surface. On removing the paper from the water, the pattern is completely printed and fixed on the surface of the paper.

Agnes Pockels is the pioneer of the science of monolayers, who began her experiments about 1882 and invented many of standard method in surface chemistry[3]. However, Irving Langmuir is accepted as the founder of the monolayer science. While working in the GE Laboratories, he developed the experimental and theoretical concepts leading to our present understanding of the behavior of monolayers. He was awarded the Nobel prize in 1932. Later, with Katharine Blodgett, he devised a new method to transfer these monolayer onto the solid substrates.

The active 1930s ended with the outbreak of the second World War. The revival came in the 1960s, when Kuhn and his co-workers began a series of works showing how one could utilize monolayers to construct precise supermolecular structures for optical and energy transfer investigations[4]. Now, we are seeing a broadened scope of both scientific and technological studies.

The preparation technique and the fundamental properties of the monolayer assembly films are to be outlined. The present status and the future scopes of technological applications will be also touched upon.

§2. Molecular assembly technique[4]

The monolayer-forming molecules possess both hydrophobic and hydrophilic end groups. If the amphiphilic balance, the balance between both end groups, is appropriate, the molecules are adsorbed at the water-air interface to form a monolayer.

The monolayer on water surface is a 2-dimensional system. It is a gas film if the surface pressure F is small enough. On enhancing F, the monolayer is transformed into a solid state. Between the gas and the solid states, one recognizes sometimes liquid states.

Of versatile versions of methods of monolayer transfer, two representatives are given here.

(1) Vertical dipping method[5]

This is often referred to as the LB technique. As shown in Fig.1, the monolayer on water surface is compressed to the solid state and transferred onto the substrate by dipping and raising it traversing the water surface vertically.

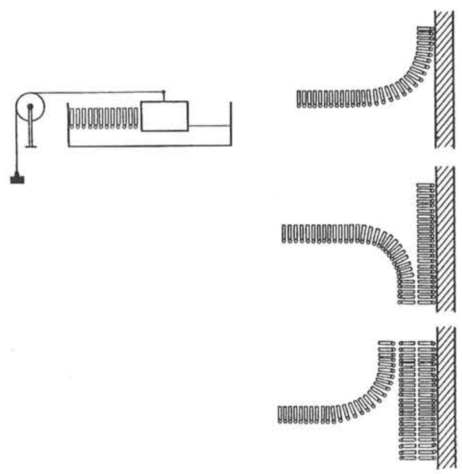

Fig.1 Schematic representation of vertical dipping method. Each molecule is symbolized with hydrophilic (o) and hydrophobic (▭) groups.

Three different types are recognized as shown in Fig.2 in the manners of deposition: a) X-type, b) Y-type and c) Z-type. As for the stability, Y-type alone is known to have persistent structure.

(2) Horizontal lifting method

This has been used in the <u>sumi-nagashi</u> art. According to K. Fukuda and his co-workers[6], this method is available also for gas and liquid films, and the resulted films are X-type.

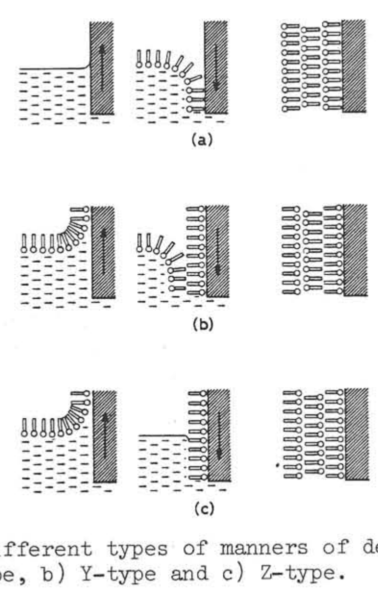

Fig.2 Different types of manners of deposition. a) X-type, b) Y-type and c) Z-type.

The molecular assembly technique, free from hard processes like heating and exposure to vacuum, is a suitable means to obtain largr area ultrathin organic films with uniform thickness and quality. Various organic materials can be used in this technique. For the supermolecular architectures, we can use "pure monolayers" and "mixed monolayers" as well. Combination of these monolayers allows us versatile "homogeneous" and "heterogeneous" systems.

§3. Versatile LB films

(1) Conventional LB films

Straight-chain fatty acids, $CH_3(CH_2)_{\underline{n}-2}COOH$ ($C_{\underline{n}}$), with $\underline{n}$=16∿22, are well-known film-forming materials. Salt films are obtained if the water contains metal ions[5]. Among these conventional films, Cd salt Y-type shows excellent structural stability as recognized by Kuhn's group.

Here we show the results of X-ray analyses of Cd salt Y-type films[7]. In the Y-structure, Cd^{+2} ions are arranged along the hydrophilic interfaces composed of $-COO^-$ ends, forming the well-contrasted bilayer unit cells. The spacing $\underline{d}$ between the adjacent Cd^{+2} planes is therefore two monolayers thick $2\underline{l}$, and related with $\underline{n}$ as,

$$\underline{d}(\underline{n})=2\underline{l}(n)=5.3+2.50\underline{n}\ (\text{Å}), \qquad (1)$$

The coefficient is comparable to the second-nearest-neighbor-distance of hydrocarbon chain (2.54Å, typically), indicating a straightened conformation of the chains with their axes normal to the layer plane. Model calculations indicate that this chain conformation is kept invariant also in the heterogeneous systems, and that each assembly system is an actual reproduction of the designed superstructure.

The Cd salt films are found to be highly insulative dielectric media[8]. For each $C_{\underline{n}}$, the dielectric constant is insensitive to both temperature and frequency.

The reproducibility of conductivity measurements was very poor until the early 1970s[9]. Mann and Kuhn[10] have demonstrated that, with careful application of the technique, one can measure the electrical transport through LB films of even one monolayer thick. In this single-layer case, the conductivity σ is found to decrease exponentially with $\underline{n}$. This, allowing for Eq.(1), leads to an expression,

$$\sigma=\sigma_0 \exp(-2\alpha \underline{l}(\underline{n})), \qquad (2)$$

derived from the theory of electron tunneling through an insulating barrier. A quantitative agreement was attained between the experiment and theory, with $\alpha \simeq 0.7 Å^{-1}$ as the wave-function damping constant.

For the $C_{\underline{n}}$ multilayer case, the conductance obeys the Ohmic law suggesting a bulk process[8]. As seen in Fig.3, σ is found to obey a similar relation to Eq.(2) with identical α but a temperature dependent σ_0[11].

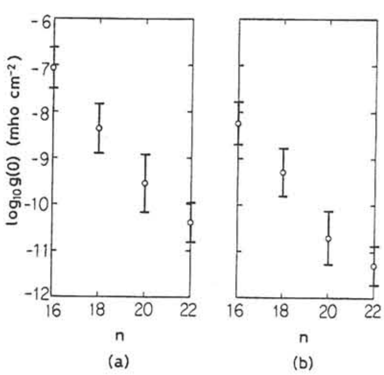

Fig.3 dc Conductance g(0) per monolayer of $C_{\underline{n}}$ multilayer. (a) room temperature, (b) 77K.

A theoretical consideration in the multilayer case has led to a hopping model as schematically given as follows[12]. Under an electric field, an electron moves about the system, sometimes along an interface, sometimes traversing the hydrocarbon barrier, to drift towards the positive electrode. The assumptions involved are; each monolayer is associated with localized electronic states at both interfaces; the transport is the thermally assisted tunneling between these states through the hydrocarbon barrier, in which the traversing rate should be governed by $\underline{l}$ and α as in the single layer case.

The advances in the electrical measurements led to the appreciation of the possibilities for device applications. G. G. Roberts et al. have demonstrated the feasibility of MIS devices, including FET, utilizing the conventional Cd salt films[13]. They have observed, for the first time in InP, an increase of capacitance in the strong inversion region. The surface state densities at the InP interface were calculated $10^{12} cm^{-2} eV^{-1}$. In addition, Roberts' group has shown that, with LB films, fairly clean surfaces are formed also on amorphous and crystalline Si, GaAs, GaP, InSb, CdS, CdTe, ZnS and (HgCd)Te[14), 15)].

(2) Unconventional LB films

(2-1) Polymerizable LB films

Certain classes of film-forming materials can be polymerized after incorporated in LB system without destruction of layer structure, ensuring the thermal and mechanical stability.

Three examples are touched upon here. G. L. Larkins et al. have recently reported Josephson junctions utilizing the monolayers of vinyl stearate, $CH_3(CH_2)_{16}COO{=}CH_2$, polymerized with ^{60}Co γ-rays[16]. Barraud et al. have demonstrated the feasibility of electron resist films of ω-tricosenoic acid, $CH_2{=}(CH_2)_{20}COOH$[17]. A thermal stability up to 230°C has been attained by the UV-irradiated LB films of diacetylene derivative, $CH_3(CH_2)_{11}$-C≡C-C≡C-$(CH_2)_8COOH$, developed by Wegner and his co-workers[18].

(2-2) Polymer monolayers

As already seen, proteins are utilized in the sumi-nagashi art. McAlear and Wehrung[19] have recently reported a new method of metal deposition using a monolayer of a synthetic protein, polylysine. Further, they have suggested that molecular aggregates can be deliberately constructed if one develops such antibody proteins that form monolayers, each retaining its specificity to the antigen molecules. The micropatterning is, according to them, carried out using electron beam by denaturing the protein molecules with irradiation. For the details, the readers are referred to Ref. 20.

(2-3) Functional LB films

Recently, various molecules have been developed aiming to obtain LB films with specific electronic functions. Such molecules are often well-known organic semiconductors substituted with side chains to ensure the amphiphilic balance. By reference to the hopping model, they are classified into three categories, the example of which is shown in Fig.4[21], that is; (I) the hydrophilic interface-modifiers, (II)the hydrophobic interface-modifiers and (III)the barrier modifiers. For the types (I) and (II), the hopping scheme is valid for the transport across the monolayers, the thermally assisted tunneling through the hydrocarbon barrier. Type (III), in contrast, introduces electronic states into the barrier to control the transport in the normal direction.

Another possibility to reduce the impedance is to shorten the side chain lengths; the development of lightly substituted film-forming moleules[22]. Roberts' group reported electroluminescent LB films of an anthracene derivative[22], and showed that phthalocyanine can form LB films even without side chain[23].

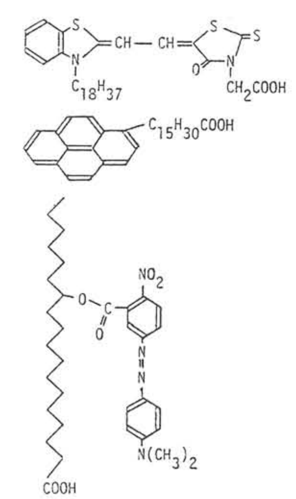

Fig.4 Examples of functional film-forming molecules.

The studies of heterogeneous LB films, although in an initial stage, are far from discouraging[24]. Saito et al.[25] have quite recently reported p-n junction photodiodes based on LB films of merocyanine and triphenylmethane derivatives. Photovoltage up to 0.7V is obtained for seven-layer films.

§4. Concluding remarks

The present review has given only the barest outline of LB films to those who are working in the field of electronics.

We are already aware of "molecular electronics" aiming to utilize the phenomena characteristic of molecular domains. This concept, at present, appears to cover a wide scope, ranging from the applications within the framework of silicon technology to bioelectronics, say, to spawn electronic circuits. In the early stages of research, however, it should be indispensable to develop new functional molecules backed by the technique to arrange them in well-defined aggregates. This process is now on the way in the field of LB film studies.

Acknowledgements

The author wish to express his thanks to Dr. S. Iizima, Dr. T. Fukui and Dr. M. Saito for their helpful comments.

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