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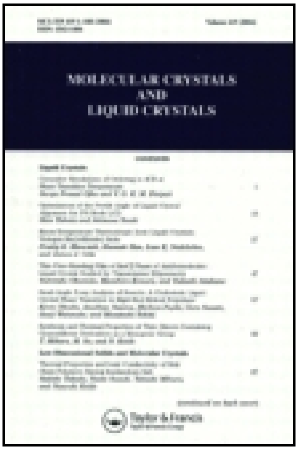

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Disclinations and Annealing in Fatty-Acid Monolayers

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Disclinations and Annealing in Fatty-Acid Monolayers

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When Langmuir-Blodgett films of 22-tricosenoic acid are annealed on a water surface, two distinct phenomena are observed. Initially, stress associated with short range orientational disorder is relieved, giving films with a 'cleaner' appearance when viewed between crossed polars and with electron diffraction patterns containing more sharply defined spots. Longer treatments, near the highest practicable temperatures, cause a significant reduction in the density of disclination defects. This observation is consistent with the identification of conducting defects with disclinations.

Keywords: Langmuir-Blodgett films, conducting defects, disclinations

1. INTRODUCTION

A number of recent studies have characterised the extrinsic conduction in metal/fatty acid Langmuir Blodgett (FALB) film/metal cells by means of their current-voltage relationship. This has been shown to be affected by penetrating filaments of top-contact metal,[1] which occur at a density of the order of 1 mm^{-2},[2,3] and whose diameter is approximately 50 nm.[3,4] It is known that the top-contact metal does not penetrate the film at random, but rather at specific points of weakness in the film which were present in the monolayer on the water surface prior to deposition. This follows from the observation of Tredgold *et al.*[5] that the conductivity of a 15-layer cadmium octadecanoate cell can be reduced by two orders of magnitude compared to conventionally deposited films by allowing the initial monolayer

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to settle on the water surface for 2 hours prior to deposition, with each of the subsequent layers of the film being deposited from a freshly-spread monolayer. The strong dependence on the preparation of the first layer implies that the points of weakness propagate into all the layers which are subsequently deposited. This is turn implies that they have a specific structure, rather than merely being small holes which would be rapidly bridged.[6] It is reasonable to assume that they have dimensions commensurate with those of the resulting metal filaments, i.e. 50 nm in diameter, an area normally accommodating 10,000 molecules approximately. Since this distance is much larger than the spacing between molecules, the points of weakness appear to be associated with long-range order of some kind in the two-dimensional monolayer. This conclusion is reinforced by the observed correlation between cell conductivity and the film disorder observed by transmission electron diffraction.[5]

The subject of long range order in two-dimensional phases is somewhat controversial. Peierls showed that the amplitude of long wavelength phonons would effectively destroy long range order,[7] but there have nevertheless been demonstrations of, for example, 2-D ferromagnetic phases.[8] This apparent contradiction has been resolved by Nelson and Halperin[9–12] who showed that, although absolute long range order does not exist in two dimensions, it is nevertheless possible to have high correlations of translational order over macroscopic distances, characterised by an algebraic, rather than exponential, decay. In addition, they showed that melting of two-dimensional phases can sometimes occur in two stages. The intermediate phase is characterised by exponential decay of translational order, but algebraic decay of orientational order. This behaviour is analogous to that of three-dimensional liquid crystals, but does not correspond to any of the established categories (cholesteric, nematic, smectic A, B, C, . . . etc). Nelson and Halperin thus proposed the names 'tetratic' and 'hexatic' liquid crystal, for such materials with 4- and 6-fold coordination respectively.

An important and characteristic feature of liquid crystalline phases is their ability to form structures with orientational discontinuities called disclinations.[13,14] Structural discontinuities of this type cannot exist in phases with long-range *translational* order, as the associated stresses would exceed the yield threshold of the material, but they do require the presence of long range *orientational* order. Orientational order has not yet been seen directly in water-surface monolayers, but it has been indirectly demonstrated by transferring the monolayer to a solid substrate and then depositing an overlayer which

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develops birefringence depending on the local monolayer orientation.[15-17] Using such methods, disclinations have been seen in fatty-acid monolayers.[18,19] Since numerous diffraction studies[20-22] have shown these monolayers to have (local) 6-fold symmetry, they must be hexatic liquid crystals.

From the results of an experiment which simultaneously shows the conducting defects and the crystalline features of a single monolayer, Peterson[19] proposed that the points of weakness are in fact disclinations. This hypothesis explains all of the previously conflicting aspects of the current-voltage observations. The measurements of Tredgold *et al.* then imply that such disclinations must slowly disappear from a monolayer on the water surface.

The aim of the present study was to compare the birefringence and electron diffraction patterns of freshly-spread and annealed monolayers and, in particular, to look for evidence that disclinations disappear. In order to eliminate possible confusion due to the long-term action of contaminants on the monolayer,[23] all of the experiments were performed on an acidified subphase. Under these conditions, octadecanoic acid monolayers are not stable enough even at 19°C, and therefore all the reported experiments were carried out with 22-tricosenoic acid.

2. EXPERIMENTAL

The details of the Langmuir trough, the water purification unit, the polarising microscope and the electron microscope used to obtain reflection high-energy electron diffraction (RHEED) have been reported previously,[24-26] as has the technique for the preparation of hydrophobic silicon substrates.[24]

The monolayer of 22-tricosenoic acid for the deposition of the initial layer was spread from CCl_3CH_3 solution to a surface pressure of less than 3 mN/m. Within one minute of spreading, the substrate was half covered with an unannealed monolayer by compressing to 35 mN/m and partly immersing the substrate.

Monolayer annealing involved heating the trough enclosure with a tungsten filament infra-red lamp energised at a constant power level for a specific period of time. During this process the surface pressure was reduced to 30 mN/m and maintained at this level and the substrate was kept half-immersed.

Following each annealing treatment, the trough was allowed to cool below 25°C. The monolayer was then recompressed to 35 mN/

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m and the remainder of the substrate was immersed to deposit some of the annealed monolayer.

Subsequent layers were deposited from a freshly-spread monolayer. For RHEED study the total thickness was 10 layers while for polarised light microscopy it was 170 layers.

The disclination density figure given was determined experimentally by counting the number of non-closed lines of discontinuity in a measured area. Since each open line terminates at one end with a disclination of rotation $+60°$, and at the other with a disclination of rotation $-60°$, the figure quoted is equal to the density of each type of disclination.

For all experiments, the subphase was acidified with HCl to a pH of less than 3. The ambient laboratory temperature was maintained at 19°C.

3. RESULTS

Figure 1 shows a photomicrograph, taken with crossed polarisers, of the boundary between annealed and unannealed regions in a sample where the monolayer was annealed on the water surface for 10 min at a maximum temperature of 22°C. It can be seen that in the annealed film the 'crystallites' appear larger and have smoother changes of

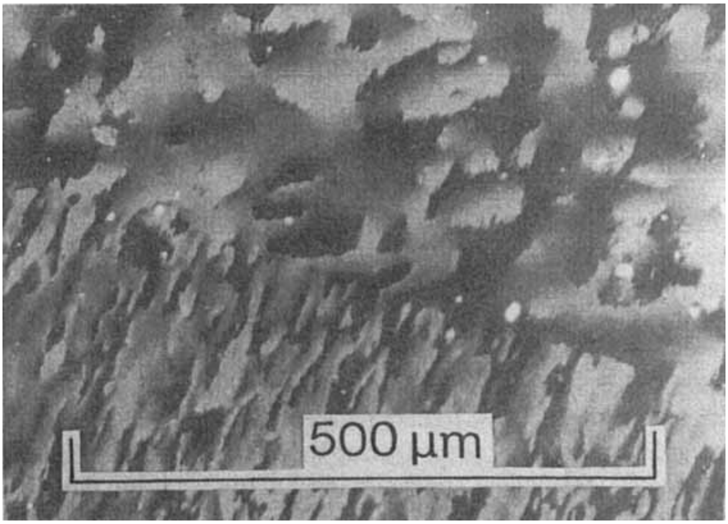

FIGURE 1 Image between crossed polars of the boundary between annealed and unannealed regions. Annealing time 10 min, max temperature 22°C.

local orientation. However, careful counting of the open lines of discontinuity in the two regions revealed no significant difference in the densities of disclinations, which were both approximately 1000 mm^{-2}.

Figure 2 gives the RHEED pattern of a 10-layer film whose initial monolayer was also annealed at a maximum temperature of 22°C for 10 min. The spots marked R and T originate from regions of orthorhombic and triclinic subcell symmetry respectively. Although the sharpness of these spots is not as pronounced as in a pattern previously reported for octadecanoic acid,[27] it is greater than in most other patterns reported for fatty acid films[22,26,28] and the near-axis R and T spots are distinct.

Figure 3 shows the birefringence image of part of a 90-minute annealed film at a magnification only half that of Figure 1. It can be seen that significant density reductions have occurred. These reductions are quantified in Table I, which gives the disclination densities measured in the regions of the film corresponding to the annealed and unannealed first layers for a number of differently treated samples. The duration, heating power and maximum temperature of each anneal is given in the same table. These results suggest that temperature is more significant than duration.

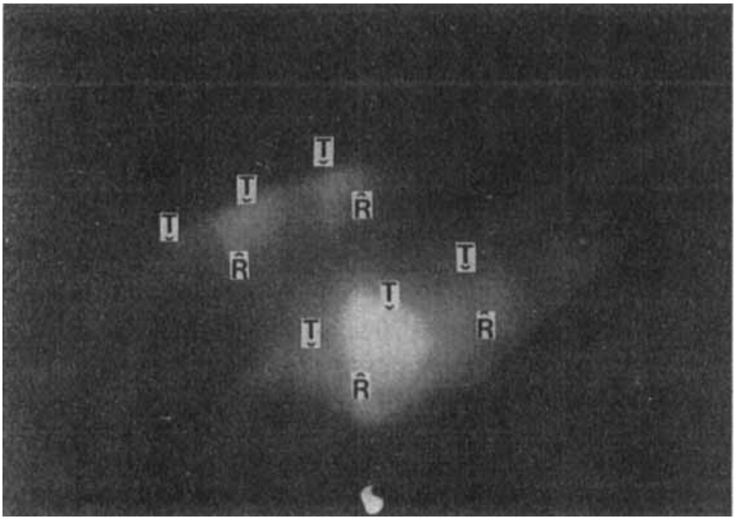

FIGURE 2 RHEED pattern of 10-layer film with initial monolayer annealed for 10 min (max. temp. 22°C).

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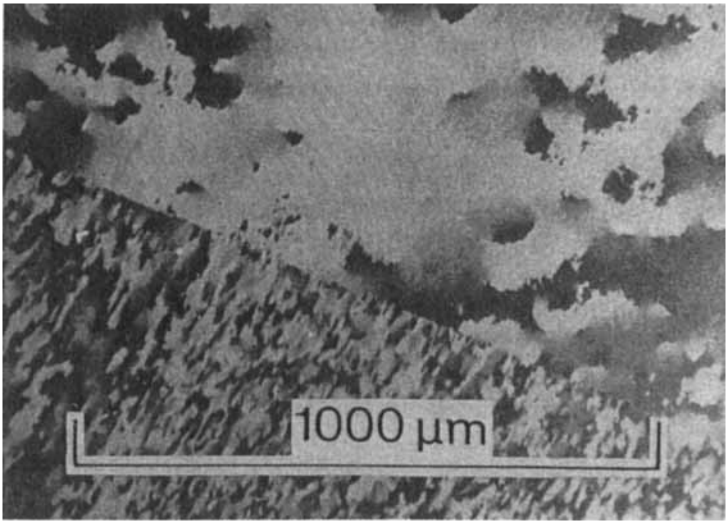

FIGURE 3 Image between crossed polars of a film showing significant reduction of disclination density on annealing. Annealing time 90 min, max. temp. 33°C.

4. DISCUSSION

The improvement of crystallinity which occurs on annealing is confirmed by the sharpness of RHEED spots shown in Figure 2. In fact, for this particular sample there was no corresponding reduction in the disclination density. Consequently, it is suggested that the first stage of the annealing process involves only the relaxation of short range perturbations of orientational order not associated with disclinations.

The values of disclination density given in Table I show distinct reductions on annealing under certain conditions. Since the phase transitions of 22-tricosenoic acid occur at higher temperatures than those of octadecanoic acid, it is plausible that a similar process should occur in the latter material at 20°C. The absence of any disclination density reduction would have been strong evidence against the identification of conducting defects as disclinations.

To summarize, this paper reports the first measurements of disclination densities in fatty acid LB films, together with definite evidence for their removal under certain conditions of annealing on the subphase before deposition is begun. Since there is strong evidence to link disclinations with defect conduction in these films,[5,19] this result is of major importance for their applications to electronics.

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TABLE I

Comparison of disclination densities of films prepared on unannealed and annealed first monolayers for the various treatments shown. The quoted error is $\pm 3\ \sigma$ and in each case, is derived from measurements of several areas on a single sample

Heating period (min)	Heating power (W)	Max. temp. (°C)	Disclination density, mm^{-2}	
			Unannealed	Annealed
3840	0	19	810 ± 220	850 ± 230
10	275	22	550 ± 300	470 ± 290
50	275	29	1500 ± 300	520 ± 180
90	275	33	900 ± 200	170 ± 60
105	275	34.5	850 ± 250	180 ± 90

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