Synthetic Metals, 60 (1993) 111–114

Conducting Langmuir–Blodgett films of hexadecyl-BEDT-TTF charge-transfer salts with inorganic compounds

Tatiana S. Berzina and Vladimir I. Troitsky
Zelenograd Research Institute of Physical Problems, 103460 Moscow (Russian Federation)

Elisa Stussi, Marcello Mulè and Danilo De Rossi
Centro 'E. Piaggio', University of Pisa, via Diotisalvi 2, I-56122 Pisa (Italy)

(Received December 11, 1992; in revised form March 18, 1993; accepted March 19, 1993)

Abstract

A method for forming conducting Langmuir–Blodgett films of charge-transfer salts based on the interaction between surfactant donor molecules spread at the air/water interface and inorganic compounds dissolved in water is proposed. Films of hexadecylbis(ethylenedithio)tetrathiafulvalene with small additions of surfactant acceptor molecules were deposited from water subphases containing $FeCl_3$ or $CuSO_4$. High quality films with conductivity of 2 Ω^{-1} cm^{-1} were deposited at pH of 3.8 when Fe^{3+} ions at a concentration of 10^{-4} M were used. In order to study the interaction of donor molecules with the compounds dissolved in water, electron probe analysis of the films was carried out. Variants of charge-transfer salt formation are discussed.

Introduction

Conducting Langmuir–Blodgett (LB) films [1] are promising components for the development of molecular electronic devices. Conducting layers can be introduced into assemblies of alternating LB monolayers [2] to provide electron transfer in horizontal planes. In addition, discovery of field effect in conducting LB layers [3] makes conductivity modulation possible by means of an external electric field. Film conductance was proved to be destroyed by electron beam effect [4]. Therefore, high resolution patterns can be created using the electron beam lithography technique. Patterning of conducting paths can be obtained in principle with much higher spatial resolution by the effect of the current of the STM tip. In order to realize such possibilities, highly conductive, uniform and stable LB films with good sensitivity to the electron beam are necessary. In the pioneering work on conducting LB films of docosylpyridinium charge-transfer salt with TCNQ [1], precursor nonconducting films with a high degree of charge transfer between pyridinium and TCNQ groups were deposited. Then, stacks of $TCNQ^-$ anions were partially oxidized by iodine to obtain conductivity. The same procedure of iodine doping was used for preparing conducting films of one-component donor molecules [5]. In many cases some uncontrolled doping took place in the process of deposition and conductance without any treatment was observed. Two-component LB films consisting of alternating surfactant donor and acceptor monolayers [6] were used in another attempt. LB films consisting of mixed monolayers of such compounds [7] were also formed to provide charge transfer between donor and acceptor molecules.

Electrically conducting polypyrrole LB films were deposited from the surface of a subphase containing ferric chloride [8, 9]. This inorganic compound was used to polymerize and oxidize the mixture of pyrrole monomer and surface active pyrrole derivative at the air/water interface, giving rise to electrical conductance. The best value of conductivity obtained was equal to 0.1 Ω^{-1} cm^{-1}.

In the present work we used a procedure for forming LB films of charge-transfer salts based on the interaction between surfactant donor molecules spread at the air/water interface and inorganic compounds dissolved in water. Conducting films of hexadecylbis(ethylenedithio)tetrathiafulvalene (C_{16}-BEDT-TTF) with small additions of surfactant acceptor molecules were deposited from water subphases containing $FeCl_3$, or $CuSO_4$ at different concentrations and pH values. Quality of the deposited films was verified by optical microscopy and conductivity was measured. Electron probe analysis of the films deposited onto ultrathin collodion substrates was carried out in order to study the interaction of donor molecules with the compounds dissolved in water.

0379-6779/93/$6.00

Experimental

Stability of one-component C_{16}-BEDT-TTF monolayers at the air/water interface proved to be unsatisfactory. For this reason, conducting films of C_{16}-BEDT-TTF mixtures with heptadecyloxycarbonyltetracyanoanthraquinodimethane (C_{17}-OC-TCNAQ) or octadecylaminosulfonyltetracyanoanthraquinodimethane (C_{18}-AS-TCNAQ) in different ratios were realized. Best transfer conditions were obtained when a ratio of 10:1 was used. Small amounts of acceptor molecules stabilize the monolayers without change in electrical properties of the deposited films [10].

Surfactant compounds were dissolved in a mixture of hexane and chloroform (2:1) in concentrations of 0.33 mg ml^{-1}. Concentration of $FeCl_3$ and $CuSO_4$ in water solutions varied from 10^{-4} to 10^{-3} M, and pH values were held in the ranges from 3.6 to 4.2 and from 4.6 to 5.2 for $FeCl_3$ and $CuSO_4$ solutions, respectively. Deposition was carried out using a LAUDA film balance with film lift unit. A compression speed of 50 cm^2 min^{-1} was used and films were transferred both on sapphire substrates with chromium electrodes and on highly oriented pyrolytic graphite (HOPG) at a transferring surface pressure of 20 mN m^{-1} and a transferring speed of 5 mm min^{-1}. Quality of deposition was checked with an optical microscope.

Voltage–current characteristics were measured by two-probe and four-probe techniques [11, 12] to determine the conductivity of the films. With the two-probe technique, we estimated quickly the value of conductivity and compared different samples during the elaboration of the technology. Substrates used for film deposition contain two interdigitated electrodes, each consisting of 50 parallel, comb-like chromium strips, with an interdigitation depth of 5 mm and a gap width between neighbouring strips of 0.05 mm. The contribution of the film/electrode junction resistance to the total sample resistance was evaluated from the comparison of two-probe and four-probe measurements carried out on films with different values of thickness and conductivity.

Because of the strong anisotropy of film conductivity in the layer plane with respect to the normal direction, current is assumed to flow preferably through the conducting planes located close to the substrate. One monolayer is not conducting. Then, the increase in film conductance is approximately proportional to the number of monolayers up to 11–13 monolayers and further depositions result in a saturation of the film conductance as a function of the number of monolayers. For this reason, films of about 11–15 monolayers were generally used for a quick evaluation of conductivity value. Then, conductivity of thicker films was calculated according to the following criteria. We took into account the current distribution between different conducting planes, measuring the characteristics of films with gradually increasing thickness. In order to compare correctly the conduction properties of our films with those of LB films of other compounds containing, for example, insulating regions of different thickness, we assigned the conductivity to the regions of BEDT-TTF fragments only. The thickness of conducting regions was estimated using structural data [7]. The four-probe technique was applied to the films deposited under optimum conditions for determining the value of conductivity with higher precision. The configuration of the evaporated chromium electrodes and the conducting areas of the films, which were deposited onto sapphire substrates, are shown in ref. 12. The required pattern of conducting area was obtained by electron irradiation of the LB film through a specially prepared mask. The same procedure described above for the two-probe technique was also adopted to calculate the film conductivity for the four-probe technique. In order to evaluate film sensitivity to electron beam, irradiation was performed with electrons accelerated under a voltage of 2.5 kV. Electron doses of 10^{-6} to 10^{-4} C cm^{-2} were used.

A KEVEX 5100 X-ray energy spectrometer combined with a JEM-100C electron microscope was used for electron probe microanalysis. An accelerating voltage of 100 kV was used in these experiments; sample tilt was equal to 35°. Lines of soft X-radiation were absorbed by a beryllium window of the detector. Analysis of light elements (lighter than sodium) was therefore impossible.

Samples for electron probe microanalysis were prepared as follows. Tantalum substrates with holes of 100–200 μm in size were covered by thin collodion films 10–20 nm thick. They were placed in special holders, which provide free access of water to the substrate backside, though preventing film deposition thereon. LB films consisting of 19 and 39 monolayers were deposited onto the substrates at a pH of 3.8 and $FeCl_3$ concentrations of 10^{-4}, 5×10^{-4} and 10^{-3} M to obtain samples with different contents of iron, as far as a certain amount of metal ions is transferred from the subphase together with the monolayer. LB films containing the same numbers of monolayers were deposited from the surface of pure distilled water as well for the preparation of reference samples. Then, definite amounts of iron from 3.5 to 15.0 μg cm^{-2} were evaporated in a vacuum chamber on the initially iron free samples. Thus, reference samples and samples under measurement appeared to be similar to each other and differed only in iron distribution along the normal to the layer plane, but this characteristic is irrelevant in these experiments, the LB films being so very thin. No corrections usually carried out in the electron probe analysis [13] were necessary for these films and quantitative data could be obtained from comparison of line intensity values. Correlation of sulfur and iron K_α lines was determined both for reference samples and samples under measurement, making quantitative comparison of iron contents possible.

Results

The use of different concentrations of $FeCl_3$ in water did not affect surface pressure–area isotherms of mixed monolayers (Fig. 1). Areas per molecule are equal to 0.35 ± 0.01 nm^2. The area per molecule for the pure donor monolayer is small because of unsatisfactory spreading. Surface pressure–area isotherms of monocomponent C_{17}-OC-TCNAQ and C_{18}-AS-TCNAQ monolayers were also recorded, giving an area per molecule equal to 0.37 ± 0.02 nm^2 (Fig. 1). Thus, area per one donor molecule in the mixed monolayer can be assumed to be equal to 0.35 nm^2 because of the little addition of acceptor compound and being area per molecule of acceptor and mixture comparable.

Subphase best conditions for film quality were found by analysing their morphology by optical microscopy. Films with minimum density of visible defects were obtained at the concentration of 10^{-4} M for $FeCl_3$ and 5×10^{-4} M for $CuSO_4$ solutions. pH values were equal to 3.8 and 4.8, respectively. A conductivity of about 2 Ω^{-1} cm^{-1} was measured for the best samples (obtained for a mixture of C_{16}-BEDT-TTF and C_{17}-OC-TCNAQ in the established ratio of 10:1 on a subphase of 10^{-4} M $FeCl_3$). Irradiation by an electron beam with a dose of 10^{-4} C cm^{-1} caused a decrease in conductivity up to 1000 times without any change in film morphology. Major doses caused a crosslinking in the film making the latter insoluble in hexane. However, upon iodine doping these areas became conducting again. The value of conductivity does not usually attain the initial value, but for some samples it is just three to for times less than the value measured before irradiation. The highest recorded value was equal to 0.5 Ω^{-1} cm^{-1}. Utilizing this phenomenon, desired patterns can be created in the conducting material without the appearance of relief on the surface, or a new lithographic process can be carried out, etching conducting zones in hexane after strong selective film irradiation.

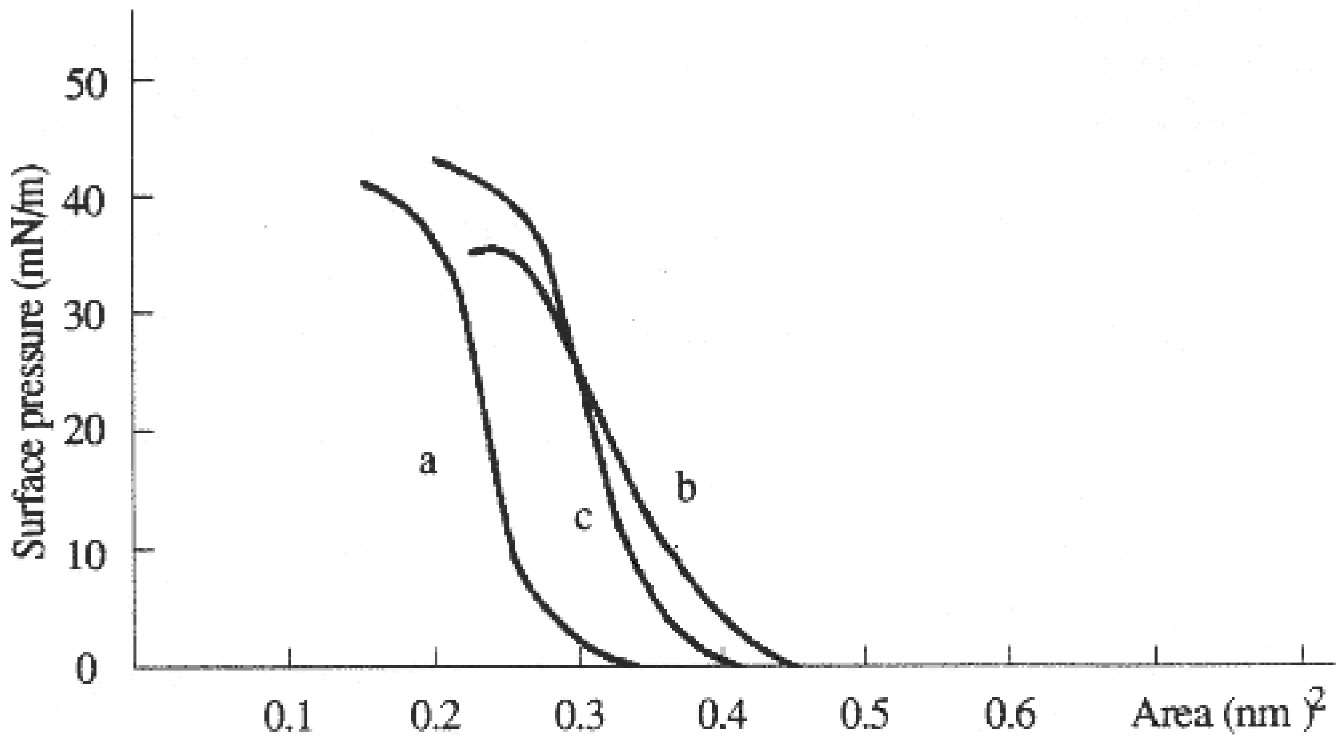

Fig. 1. Surface pressure–area isotherms of C_{16}-BEDT-TTF (a), C_{17}-OC-TCNAQ (b) and their mixture in the ratio of 10 to 1 (c) (at $FeCl_3$ concentrations of 10^{-4}, 5×10^{-4} and 10^{-3} M).

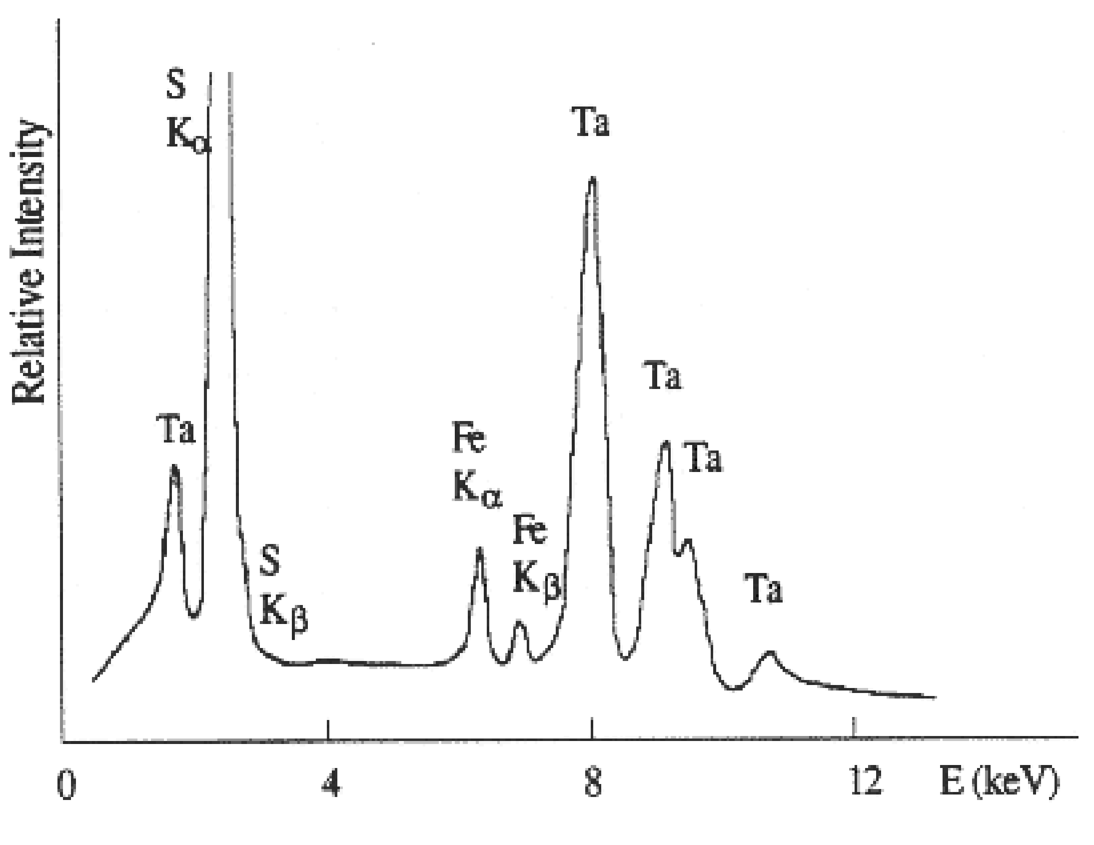

Fig. 2. X-ray spectrum of 39 monolayers of C_{16}-BEDT-TTF mixture with C_{17}-OC-TCNAQ deposited at a pH of 3.8 and $FeCl_3$ concentration of 10^{-3} M.

X-ray spectra (Fig. 2) were always stored up to a definite value of sulfur K_α line integral intensity. When carrying out electron probe analysis, the dependence of iron K_α line intensity on the surface density of evaporated material for standards was first measured. This dependence appeared to be linear and could be extrapolated to the point of intersection of the coordinate axes. Thus, it was certain that all evaporated metal was accumulated in the film. Iron surface densities in the samples under measurement were calculated using this calibration curve and reported in Table 1 together with the number of C_{16}-BEDT-TTF molecules per iron ion. The latter was calculated proceeding from measured areas per donor molecule and taking into account that some part of the monolayer area is occupied by acceptor molecules. As can be observed, the number of C_{16}-BEDT-TTF molecules per iron ion varies approximately from three to nine depending on $FeCl_3$ concentration; thus, one of these donor molecules can interact with one iron ion. No chlorine ions were detected in the film.

TABLE 1. Results of electron probe microanalysis

Concentration of $FeCl_3$ in solution (M)	Surface density of iron ions in monolayer (cm^{-2})	Number of donor molecules per iron ion
10^{-4}	$(0.13 \pm 0.02) \times 10^{16}$	6.9 ± 1.7
5×10^{-4}	$(0.14 \pm 0.02) \times 10^{16}$	6.3 ± 1.2
10^{-3}	$(0.24 \pm 0.03) \times 10^{16}$	3.7 ± 0.7

Discussion

The same films deposited from the surface of pure water are conducting [8], which can be explained with some uncontrolled doping. The value of conductivity is usually equal to 0.01–0.1 Ω^{-1} cm^{-1}. Introduction of $FeCl_3$ into water increases conductivity up to 0.5–2 Ω^{-1} cm^{-1}, depending on technological conditions. The initial supposition that interaction between donor molecules and Fe^{3+} ions can take place due to capability of transfer of iron ions from the Fe^{3+} into Fe^{2+} form with formation of some charge-transfer salt between donor molecule and iron ion seems to be confirmed, because strong increase of conductivity takes place as iron is present in the multilayer. Moreover, the same phenomenon was observed when copper ions were introduced into water solution, probably changing their state from the Cu^{2+} to Cu^{+} form, while nothing happened when, for example, Ba^{2+} ions were used. Analysis for copper could not be fulfilled because of the presence in the spectra of copper lines caused by electron scattering in a column of the microscope and in the holder.

High quality of the multilayers obtained during film transfer is possible only when the monolayer at the air/water interface is in a neutral state. Thus, three anions must be coordinated with each $(C_{16}\text{-BEDT-TTF})^{+}Fe^{2+}$ pair in the LB film after deposition. The only variant for our case was the interaction with three OH^{-} ions, as chlorine lines were absent in the spectra.

We suppose that the mechanism of interaction of hydroxyl anions with the charged monolayer is the following. The concentration of $FeOH^{2+}$ ions in the solution at a pH of 3.8 can be evaluated with the equation for ion activity [14]:

$$\log([FeOH^{2+}]/[Fe^{3+}]) = -2.43\text{pH}$$

According to this equation the concentration of $FeOH^{2+}$ ions is very small. The concentration of $Fe(OH)^{2+}$ ions will be considerably less. However, concentration of hydroxyl anions near the charged monolayer is much more than that in bulk and the effective pH value is higher. For this reason, the most probable situation is that two OH^{-} anions are linked by chemical bonds with Fe^{2+} ions resulting in $(C_{16}\text{-BEDT-TTF})^{+}Fe(OH)_2$ cation formation (actually $(C_{16}\text{-BEDT-TTF})^{+(1-\delta)}Fe(OH)_2{}^{+\delta}$, where δ depends on the degree of charge transfer). The third OH^{-} group can be located in arbitrary order near the monolayer. Undoubtedly, other variants of monolayer interaction with OH^{-} ions are possible. Formation of two or three donor–acceptor bonds between Fe^{3+} ions and donor molecules is hardly probable because of the expected large distances between the latter, which can be evaluated from the area per molecule.

Conclusions

The charge-transfer salt preparation method proposed in the present work broadens considerably the number of combinations of usable compounds, since many chemical elements can possess variable valency. In contrast with classical methods of organic metal crystal formation, which use non-surfactant donors and inorganic compounds, in the case of the LB technique the technological procedure is simplified because any water-soluble inorganic compound can be used. In addition, it is known that many organic superconductors are obtained in a similar way. The application of the LB technique for producing films of such type can give some perspectives in the search for superconductivity.

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