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Langmuir–Blodgett films in the development of high temperature single electron tunneling devices

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Abstract

Mixed Langmuir–Blodgett (LB) films consisting of inert molecular stearic acid matrix and embedded cluster molecules (carborane and organo-metallic molecules) were used to create reproducible, stable, ordered, planar nanostructures with different systems of electron tunnel junctions. All clusters were chemically synthesized and hence had atomically equal structure and reproducible properties. Mixed monolayers on the water surface were studied. Formed molecular structures were studied at room temperature using scanning tunneling microscopy and effects related to single-electron tunneling and energy quantization of electrons were observed in such structures. © 1998 Elsevier Science S.A. All rights reserved

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1. Introduction

The development of high technologies tends to direct physical and interdisciplinary investigations into the field of mesoscopic and nanometer-scale systems. Future progress in electronic and information technologies will be determined by creating nano-sized functional elements and quantum devices working at room temperature. In development of nanoscale electronic devices, such as nanoelectronic digital circuits, single-electron charging effects and quantum-size effects in isolated conducting nanoparticles are of principal importance. Each of these effects can be detected when the charging energy and/or the electronic level separation exceed the thermal energy, k_BT. The manifestation of both effects correlates, as a rule, with decreasing nanoparticle size. Relevant effects were observed at room temperature in the tunneling current–voltage characteristics in a number of molecular and nanoparticle systems [1–8]. The principal point in these studies is the complete characterization of formed structures, because random variations of the nanoparticle size and/or shape can lead to unpredictable and irreproducible changes in the parameters of the tunnel system.

We have proposed an approach based on the use of mixed monolayer Langmuir–Blodgett (LB) films consisting of inert amphiphyle molecular matrix and guest cluster molecules, to create a reproducible stable planar nanostructure with different systems of electron tunnel junctions. The double tunnel junction (DTJ) structure, ‘graphite substrate-carborane cluster-STM tip’, was studied [3,7] and a corresponding molecular single-electron tunneling (SET)-transistor was demonstrated at room temperature [9].

In present work, the various nanostructures, based on the multicomponent LB films of stearic acid (SA) and a number of incorporated cluster molecules, have been studied by a scanning tunneling microscopy (STM) technique at room temperature. All clusters were chemically synthesized, and hence had atomically equal structure and reproducible properties. Mixed monolayers on the water surface have been studied. The effects related to single-electron tunneling and energy quantization of electrons were observed in formed molecular structures.

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2. Experimental details

Stearic acid (CH_3–$(CH_2)_{16}$–COOH) was obtained from Serva and used without further purification. Water was purified by a Milli-Q system (Millipore).

The cluster molecules used: carborane ($C_2B_{10}H_{12}$); organo-metallic cluster molecules of the close types: $Pt_4(CO)_5(P(C_2H_5)_3)_4$ cluster I, $Pt_5(CO)_6(P(C_2H_5)_3)_4$ cluster II, $Pt_5(CO)_6(P(C_6H_5)_3)_4$ cluster III. All clusters were synthesized by S.P. Gubin in accordance with known procedures [10]. Organo-metallic clusters have a metal nucleus surrounded by an organic coating [10]. It provides the stability of cluster structure and tunnel barrier with fixed parameters. All clusters used are diamagnetic compounds, easily dissolved in non-polar solvents, such as chloroform.

Surface pressure–monolayer area (*P–A*) isotherm measurements and monolayer transfer to solid substrates were carried out on a fully automatic conventional Teflon trough at 18–20°C as described elsewhere [11]. Langmuir monolayers were formed by spreading a chloroform solution of clusters or their mixtures with stearic acid (2×10^{-4} M) on the surface of purified water (pH = 5.9). After complete solvent evaporation, the floating monolayers were compressed by a mobile Teflon barrier at a speed of ~3 A^2/SA molecule per minute. Monolayers were then deposited onto high oriented pyrolytic graphite (HOPG) substrate at a constant pressure (19–21 mN/m), temperature and dipping speed, using the conventional horizontal lifting method with good transfer ratios.

The STM topographic measurements of the monolayer films deposited on a HOPG surface were performed using a Nanoscope-1 scanning tunneling microscope in the constant current mode. The cluster molecules were studied spectroscopically by recording tunneling current–bias voltage (*I–V*) curves in double tunnel junction geometry, where the cluster is coupled via two tunnel junctions to two macroscopic electrodes (HOPG substrate and the tip of a STM). The measurement procedure consisted in obtaining a topographic image, and then positioning the tip above an isolated cluster molecule for the tunneling spectroscopy measurements.

3. Results and discussion

Hydrophobic carborane clusters are not self-assembling amphiphylic molecules, and insoluble condensed films of carborane were not formed at the air–water interface. The surface pressure did not exceed 3 mN/m during compression of carborane spread on the water surface. Fig. 1a shows the surface pressure–area isotherm of cluster III on water subphase at 20°C. This isotherm course is typical for clusters I, II and III and it implies that these clusters by themselves form Langmuir monolayers on the water surface, in which *P* achieves values up to 40 mN/m on compression. However, those monolayers are barely transferable to HOPG substrates by horizontal or by vertical lifting methods, and STM shows only disordered individual cluster aggregates on the substrate surface.

Mixed monolayers, consisting of SA and clusters I, II and III, reveal complex behavior, not typical for mixed monolayers with immiscible components, where monolayer properties are a weighted mean of the individual values [12,13]. Fig. 1b shows the *P–A* isotherms of cluster III, mixed with stearic acid in different ratios, on water subphase at 20°C. The shift of *P–A* isotherm when the cluster/SA ratio is small (curve 2) substantially exceeds the individual potential contribution of clusters to the area. At higher cluster/SA ratios, the changes in the *P–A* isotherm diminished; this may indicate a limited inclusion of clusters in the monolayer. The average limiting molecular area for mixed monolayers of carborane with SA was 20 Å^2. Taking the area of SA (20 Å^2) into account, this implies that most of the carborane molecules at high surface pressure were squeezed out of the film onto the hydrophobic methyl groups of SA. This behavior of hydrophobic carborane is similar to that of fullerene in fullerene/fatty acid mixed monolayers [14,15].

STM allows one to visualize the molecular nanostructures and to study electron transfer processes through single molecules. The molecular structure of samples for investi-

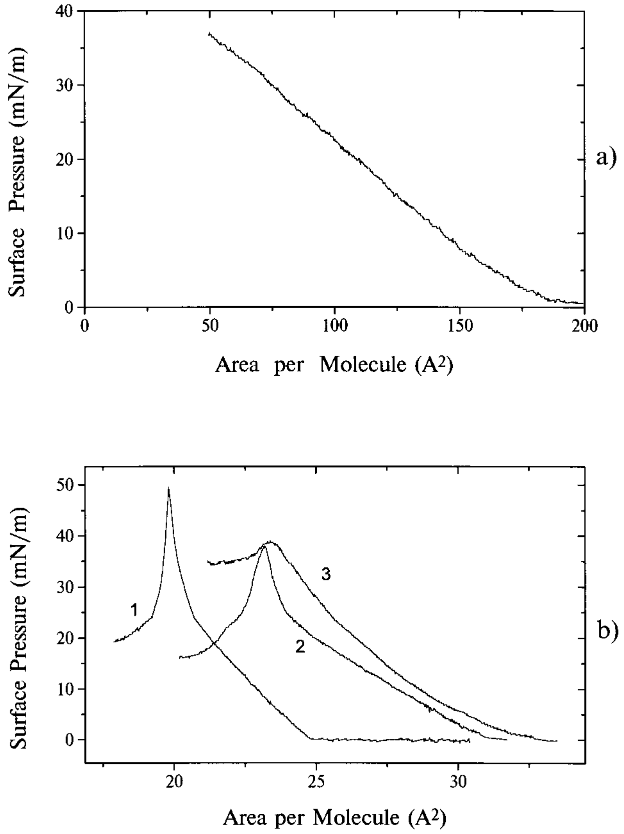

Fig. 1. (a) *P–A* isotherm of molecular organo-metallic cluster $Pt_5(CO)_6(P(C_6H_5)_3)_4$ (cluster III) on water subphase; (b) *P–A* isotherms of mixed monolayer of cluster III with SA. Curve 1: monolayer of SA without clusters; curve 2: ratio cluster/SA was 1:80; curve 3: ratio cluster/SA was 1:7. Area is calculated per molecule of SA. *T* = 300 K.

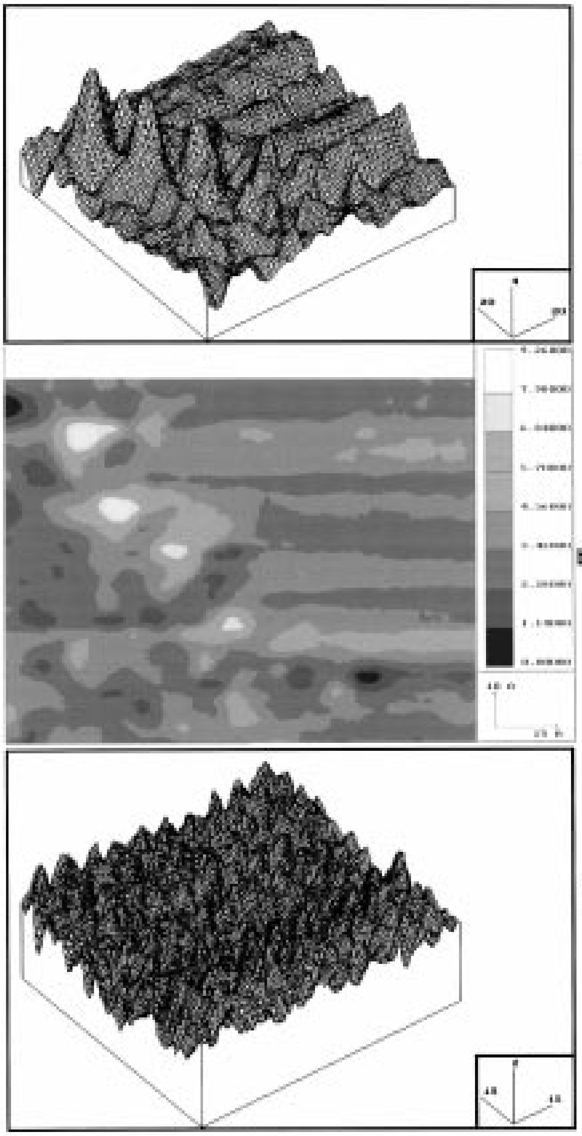

Fig. 2. STM topographic images of mixed monolayers of molecular organo-metallic clusters with stearic acid deposited by Shaefer's method onto the surface of graphite substrate. (a) 3D image and (b) top view of a chain of cluster molecules $Pt_4(CO)_5(P(C_2H_5)_3)_4$ (cluster I) in mixed monolayer of cluster I with stearic acid ratio 1:80. (c) 3D image of 2D array of cluster molecules $Pt_5(CO)_6(P(C_2H_5)_3)_4$ (cluster II) in a mixed monolayer of cluster II with stearic acid ratio 1:20. The scales of images are shown in the right bottom corner of pictures. $T = 300$ K.

gations of single nanoparticles by this technique has to be the monolayer on the conducting substrate. Fig. 2 shows topographic STM images of different mixed SA/organo-metallic cluster monolayers with characteristic observed structures: a chain of cluster I molecules (Fig. 2a,b), high ordered two-dimensional array of clusters II (Fig. 2c). The single cluster molecule and groups of clusters were also observed. Images of mixed carborane/SA monolayer (molar ratio 1:20) were similar to shown on Fig. 2c. The STM image of cluster molecules corresponded qualitatively to the size of molecule known from the structural data (diameter ~10 Å) [10].

Spectroscopic results, namely the *I*–*V* and d*I*/d*V* characteristics are shown in Fig. 3. The curves with steps of variable widths and heights (the typical one is shown on Fig. 3a,b were observed only on the organo-metallic clusters, whereas identical smooth *I*–*V* curves without noticeable particular features (Fig. 3c) were obtained everywhere else except over the cluster molecules. The *I*–*V* curve shown on Fig. 3c is characteristic for single tunnel junction 'STM tip-substrate' and its super linear course is usual for tunnel junctions [16]. All *I*–*V* curves obtained on different

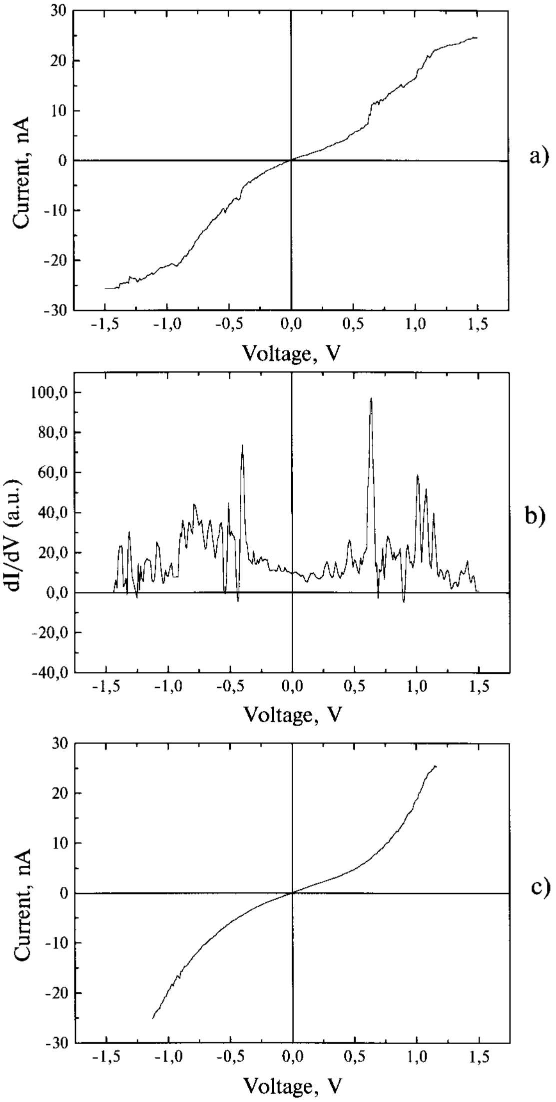

Fig. 3. STM tunneling current–voltage (*I*–*V*) characteristics of mixed monolayer of cluster molecules $Pt_4(CO)_5(P(C_2H_5)_3)_4$ (cluster I) with stearic acid ratio 1:80 recorded in double tunnel junction system 'STM tip-monolayer-graphite substrate' at 300 K. *I*–*V* curves were recorded while temporarily disconnecting the feedback circuit, and therefore, with constant tunnel junction parameters. During the *I*–*V* measurements topographic images were monitored regularly to ensure that the tip and the cluster did not drift apart. Electrons flowed from the tip to the substrate for positive *V* values. (a) Characteristic *I*–*V* curve recorded on the cluster, (b) tunneling spectroscopic d*I*/d*V* curve corresponding to curve (a), (c) typical *I*–*V* curve recorded on the monolayer surface without organo-metallic clusters and on the mixed carborane/stearic acid monolayer.

points of carborane/SA monolayer surface (including clusters) were practically identical to the one presented in Fig. 3c, resembled those for single tunnel junction and pointed out the close direct electronic contact of carborane molecules with the graphite substrate. The same effects are known for fullerene molecules deposited onto metallic substrates [8]. The conductivity (d*I*/d*V*) curve (corresponding to the *I*–*V* curve (a) in Fig. 3) is presented on Fig. 3b, and apparently reveals the complex molecular level structure of ionized cluster states in processes of DTJ tunneling. This *I*–*V* curve is determined by the tunnel junction parameters, the energy separation of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and its combination with Coulomb single-electron charging effects during tunneling. The *I*–*V* picture can be complicated also by molecular orbital anisotropy when the tunneling current is correspondingly dependent on the tip position over the molecule and on the molecular space orientation with respect to the substrate surface. To describe quantitatively the course of the DTJ *I*–*V* curve, it is necessary to solve corresponding quantum-mechanical problem taking into account the foregoing circumstances.

The curves with steps (the typical one is shown on Fig. 3a,b may be interpreted as a result of single-electron tunneling in the DTJ system. The size of the cluster is about 1 nm and the capacitance of the tunnel junctions can be estimated as 0.5 aF (5×10^{-19} F) [3]. This value gives the value of Coulomb blockade about 0.5 V which is close to the experimental value (Fig. 3a). From the Fig. 3b one can see that the steps on the branches of the *I*–*V* curve are close to periodic with the period of about 350 mV. This value is consistent with the results of the work in which the period of steps on *I*–*V* curve of molecular SET transistor on the base of twice larger cluster was approximately twice smaller [9]. These facts give evidence that steps on the *I*–*V* curves may be due to the SET effects.

4. Conclusions

The approach based on the use of mixed LB films consisting of inert molecular matrix and cluster molecules is effective for formation of reproducible, stable, ordered planar nanostructures with different systems of electron tunnel junctions. The effects of single electron tunneling and/or discrete electronic levels spectrum can be observed and studied in such structures at room temperature.

Acknowledgements

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