ECCL – Short-term Scientific Mission

Scientific report

"Low-energy electron interactions with phospholipids and their complexes"

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Host: Dr. Andrey Turchanin and Prof. Armin Gölzhäuser, Laboratory for Supramolecular Systems, University of Bielefeld, Germany
Dates and duration of the visit: 04.03.- 19.03.2009. (16 days)
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Purpose of the visit

The purpose of the proposed two-week research visit was to combine the facilities and the expertise of the two ECCL member laboratories (The Open University and the University of Bielefeld) in performing the X-ray Photoelectron Spectroscopy measurements on thin mono- and bi-layer films of phospholipids deposited on the conductive solid substrates, i.e. gold-coated mica and bare boron-doped silicon wafer. The goal of the study was to look at the change of the properties of DOPC and DPPC after irradiation with the electron beam of the energy between 2 and 1000 eV. We are seeking information about the suitability of these films as a potential substrate for deposition of another set of molecules, such as amino-acids, short peptides and oligonucleotides, all of which are basic constituents of the cell. The results are intended to answer questions related to the radiation effects on the live tissue and self-assembling properties of the biomolecules extensively used in bio-nanotechnology.

Experimental procedure

Measurements of the X-ray photoelectron spectra were performed on the OMICRON XPS-STM apparatus containing a monochromatic X-ray source (Al K_α; 1.486 keV). Samples were prepared outside the experimental setup, in air conditions, and transported into the main vacuum chamber through the load-lock system. The base pressure of the main vacuum chamber was of the order of 10^{-11} mb. The system also contains the flood gun capable of producing electrons of the energy up to 2 KeV, but with no collimation below 50 eV.

Samples were thin films of DPPC molecules deposited on two different substrates – silicon wafer and gold-coated mica. Silicon wafer was first treated with HF to remove the oxide layer from the surface and then treated with either HNO_3 or NaOH, in order to produce the hydrophilic surface

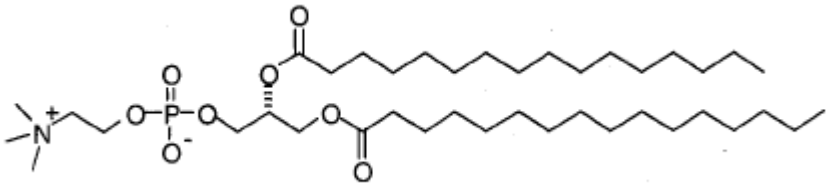

Figure 1: DPPC molecule consisting of two hydrophobic alkene chains and the polar hydrophilic head.

for binding the heads of DPPC (1,2-Dipalmitoyl-sn-glycero-3-phosphorylcholine; figure 1). Additionally, a few silicon substrates were baked in air in the furnace at 500 ^{o}C for two hours, before etching with HF and treatment with the acid or base. The reason for this was the presence of unidentified peaks in the XPS spectrum of the original silicon wafers. To accommodate analysis of oxygen peaks in the XPS spectrum from DPPC, we have also used bare (non-thiolated) gold substrates (300 nm on mica); therefore, with physisorbed molecules in the film. Preparation of all samples followed the same deposition routine consisting of ozone plasma cleaning for 12 min, rinsing with ethanol and submerging the substrates in the 20 M solution of DPPC in dehydrated absolute ethanol for 5 min. Samples were then taken out from the solution and left to dry in air for a few minutes (until alcohol evaporated and left the thin film of DPPC on the top surface). They were then transferred to vacuum, and stored in the carousel for measurements. Each sample was first scanned – survey spectrum and C 1s, O 1s, N 1s, P 2p bands – for the record of initial conditions of bonds, then irradiated with electrons of either 20, 50, 100, 200, and 500 eV, and finally the XPS spectra taken to detect the damage to the DPPC film from the electron beam.

Identification and deconvolution of the peaks have been done according to the in-built atomic binding energies in the acquisition software EIS Sphera, and the NIST XPS data base (http://srdata.nist.gov/xps/Default.aspx).

Results

Silicon wafer

Clean silicon wafer showed very broad peaks around the 116 eV binding energy and some additional peaks, possibly satellites, in the Si 1s and 2p bands. This is almost certainly the result of contamination from manufacturing (closest BE belongs to Al_2O_3 which is used for polishing glass surfaces). Also, the SiO_2 peak from the treatment of silicon wafer with NaOH or HNO_3 was too intense to allow for satisfactory deconvolution of the shifted oxygen 1s peaks from the P-O and C-O bonds (figure 2). Therefore, part of the analysis regarding changes in oxygen bonds after electron irradiation has been impossible. Carbon 1s, nitrogen 1s and phosphorous 1s shifts in binding energy, originating from different bonds in the DPPC molecule were still possible to analyze. An example of the carbon bonds being affected by irradiation by the 100 eV electron beam is shown on figure 3 a, b. The peak

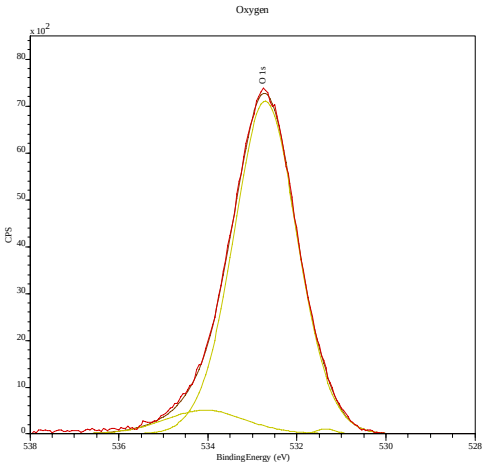

Figure 2: O 1s on hydrofilized silicone wafer

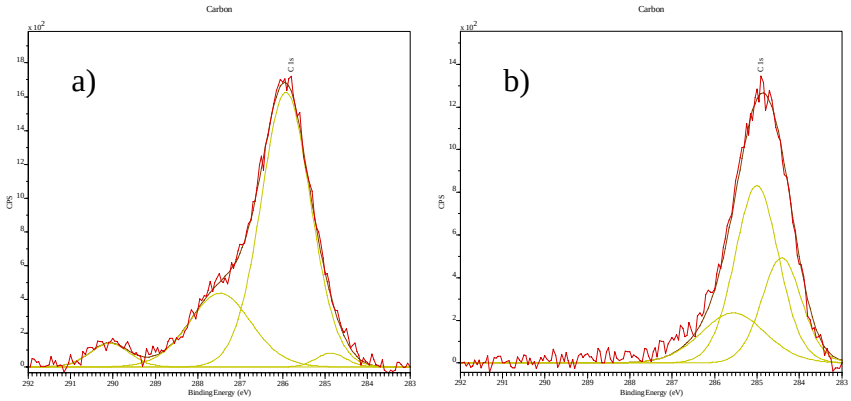

Figure 3: C 1s band with different Gaussian-Lorentzian peaks in the deconvolution, corresponding to COO-, C-C, C-O, and C-N bonds; a) before irradiation, b) after irradiation with 100 eV electrons.

at BE 290 eV corresponding to the carbonyl group COO- bond completely disappears from the spectrum, while the peak at BE ~ 285 eV corresponding to C-H (un-shifted C 1s) becomes bigger. This is only a preliminary analysis and further measurements and analysis is needed to properly characterize the effect of the electron beam on DPPC films.

Gold-coated mica

In contrast to the measurements on silicon, gold substrate allowed the deposition of the DPPC molecules only as a disordered, physisorbed films. Nevertheless, the measurements were successful and the changes in chemical bonds inside the DPPC of all relevant elements could be observed. An

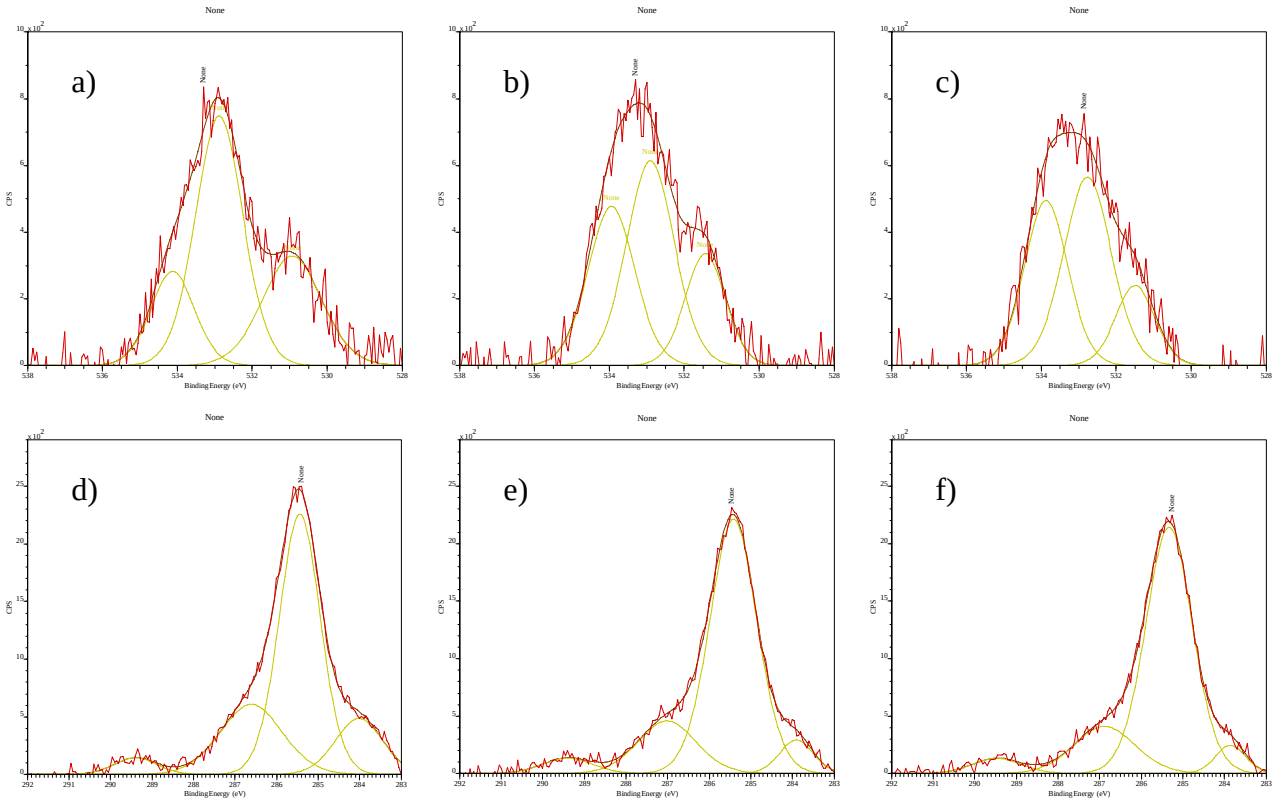

Figure 4: XPS of DPPC on gold coated mica before (a, d) and after (b, c, e, f) irradiation with 20 eV electrons; a) O 1s band from fresh sample, b) O 1s band after 5 min of irradiation, c) O 1s band after 10 min of irradiation, d) C 1s band from the fresh sample, e) C 1s band after 5 min of irradiation, f) C 1s band after 10 min of irradiation. Provisional deconvolution has been done using the NIST XPS data base (http://srdata.nist.gov/xps/Default.aspx) for the P-O-C (532eV), O-C (531.65eV), C-O-O- and C-O-N-O (534.38 eV) bonds in the oxygen band and the COO- (289.4 eV), C-C (287 eV), C-H (285 eV), and C-N-C (283.9 eV) bonds in the carbon band.

example of the effects of 20 eV electrons on these films are presented in figure 4 a-f. Changes in bonds are obvious and particularly prominent in the case of C-O bond in the oxygen band. For other electron energies, effects are very similar, except in the case of 500 eV where the damage is smaller and mostly in the carbon band. Since it is expected that the electrons of this energy produce a significant number of secondary electrons, it will be necessary to repeat these measurements in order to verify their validity.

Future plan

Further investigation of the effects of the electron beam irradiation of DPPC films will be directed towards production of a more uniform mono- and bi-layer films by using the Langmuir-Blodget deposition method and better control of electron irradiation by using a tunable electron gun instead of the present flood gun. An attempt will be made to perform the same experiment with electrons of energy below 20 eV. With more detailed analysis and improved experimental procedure in further measurements (planned in the next month), these results will be presented this year at the ECCL conference in Istanbul and the ESF-EMBO conference in Costa Brava and will be published soon after.

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