
Comparison of Change in Surface Structure of POPC Surfactant Bilayer on Si Substrate with MIES & UPS

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Abstract: Nanoparticles in the recent times have drawn more attention in the field of electronics and in particular their property of self assembly over another material surface makes them a suitable component in the development of Nanoscale materials. Self organization property of Nanoparticles has opened up whole new possibilities in the construction of 2D nanostructures through deposition of organized bilayer of surfactant called black films on a solid substrate. Newton Black Films which are much thinner than a Common Black Films attracted more interests recently with their ability to form more complex structures. In this article, Newton Black films of POPC (1-palmitoyl-2-oleoyl-phosphatidylcholine) surfactant is formed and deposited on a solid substrate after a certain amount of time and their surface structure were analyzed with time. The experiment is conducted at three different drainage states; un-dried, un-dried with a salt present, and dried; their results are compared with MIES and UPS spectrum. Where, MIES spectra being more sensitive towards surface modification show that the structure becomes more ordered with drainage time and the process gets even faster with the addition of a salt. Comparatively, in MIES the presence of new elements is more clearly observed with the variation in their energy spectra on the drained film substrate than in the un-drained substrate owing to the fact that the drained film has more patterned outermost layer comprised with the new elements.

Keywords: Nanoparticles, Self Assembly, Newton Black Films, POPC Surfactant, Metastable Induced Electron Spectroscopy, Ultraviolet Photoelectron Spectroscopy

1. Introduction

Nanoscale materials acts as a key in the development of miniaturized electronic and optoelectronic devices. These devices are designed on the foundation of the fact that the self assembly of nanoparticles over the surface and interface of another material as a consequence of their dimension are capable of displaying fascinating electronic and optical properties. These properties make nanoparticles an ideal component in the development of nanoscale materials. A lot of researches going on in the past few years regarding this self organization property over a surface, in order to construct a functional interface [1]. Whereas in the recent years, research on the self organization property of surfactants and nanoparticles resulted in certain promising outcome towards construction of 2D and 3D nanostructures.

2D nanostructures can be formed by deposition of organized bilayer of surfactants called Black films on solid substrates [2]. These black films are simply a bubble like

structure in the form of a thin film composed of a water layer sandwiched between two layers of amphiphilic molecules with their hydrophobic moieties directed outwards. They are called black films because of their transparent appearance, when the visible light is reflected at each interface and interferes destructively [3]. Newton black films are of much interest in Nanostructures than the Common black film because of the reason that Newton black films are much thinner and contain only residual hydration water in the core upon maximal drainage. It is also reported that the Newton Black Films structure can be used for ordering of complex structures like polymers etc. and it is generally done by physical process like diffusion process or electrostatic force [4]. Insertion of nanoparticles into the surfactant is also done in the same way, since these driving forces are independent of the nature of the object being inserted; nanoparticles which are made water soluble by a specific surfactant are a perfect candidate for this type of process.

So far these Newton Black Films are analyzed in its free

standing form by X-ray photoelectron spectroscopy, Atomic Force Microscopy and other means due to its high fragility but in order to render these films for practical application, it is vital to transfer them onto a solid substrate [5]. Recently, methods by which this black film can be deposited on a solid substrate are developed for more fundamental characterization. In this method a hydrophobic solid substrate is brought in contact with the Newton Black Film [6] and due to the strong adhesion force, a large area of black film is transferred to the surface with its molecular assembly preserved [7, 8].

The main objective of this experiment is to record the change in surface structure with time of POPC surfactant deposited on a Silicon substrate. The Newton black film method used here aligns the surfactant particles in an orderly manner over the film and so after the deposition the film is transferred with no loss of molecules or no change in their orientation. The deposition is done at three different drainage states, giving the film varied time to dry in order to see any structural change.

2. Materials & Methods

2.1. Newton Black Films

Newton Black Films of POPC surfactant is studied and the surfactant concentration is raised from its original concentration to 3×10^{-4} mol/g i.e. 5 times higher than the micelle concentration in order to form surfactant films as, surfactants only above their micelle concentration forms micelles. The experiment is performed through inducing air into the surfactant thus allowing them to form a micelle bubble on a glass substrate. The formed micelle is allowed to standstill with any disturbance thus providing them with the time and environment to drain thus transferring into a Newton black film.

The Newton black films are formed with this surfactant standardized in Formamide and the films are allowed to drain for two different periods i.e. 5 min. (un-dried state) and 30 min. (dried state), transferred and then analyzed. Another analysis with this POPC Surfactant at same concentration and NaI salt at 10^{-1} mol/kg is standardized in Formamide and analyzed.

The analysis involves comparison of dried, undried and undried with NaI samples. The analysis is done in a Metastable Induced Electron Spectroscopy described below and the results are compared.

2.2. Piranha Solution

Piranha solution is 3:1 combination of H_2SO_4 and H_2O_2 solution. The silicon substrate is immersed in it for nearly 15-30 minutes to clean all the impurities and then treated with Acetone and dried using Nitrogen gas.

2.3. Si Substrate is Made Hydrophobic

The silicon substrates used are 0.5cm in diameter and is around 200 μm thickness. It has to be made hydrophobic

for the black film to be transferred and is done by 40% NH_4F treatment but before that the substrate has to be cleaned properly in order to get rid of any impurities on the surface of the Si Substrate, as these impurities may affect the film transfer. After the Piranha solution treatment, the Si substrate is made hydrophobic by immersing in 40% NH_4F aqueous solution for nearly 20 min, cleaned with pure water and dried in Nitrogen gas. This treatment produces a smooth hydrophobic silicon surface suitable for film transfer.

3. Experimental Procedures

The experiments were done using MIES/UPS at base pressure (1×10^{-10} Torr) in an ultrahigh vacuum (UHV) chamber. MIES/UPS spectra were measured simultaneously using a cold-cathode discharge source for the production of metastable $\text{He}^*(3\text{S}/1\text{S})$ ($E^* = 19.8/20.6$ eV; intensity ratio 7:1) atoms with thermal kinetic energy and HeI photons ($E^* = 21.2$ eV) for ultraviolet photoelectron spectroscopy (UPS). Time of Flight technique is used in order to separate the spectral contribution from metastable and photons. MIES and UPS spectra were acquired with the photon/metastable beams incident at 45° with respect to the surface normal and utilizing a double pass cylindrical mirror analyzer (CMA). From the width of the Fermi edge the resolution of the analyzer is estimated to be ~ 0.4 eV.

Sample Preparations:

POPC surfactant standardized in FA:

POPC at 5 times cmc = 0.3 m mol/g

Mol. Wt. of POPC = 760 g/mol

Volume of FA = 80 ml

Amount of Substance = 20.66 mg (Mass of POPC from calculation)

Amount of Substance = 20.64 mg (Mass of POPC weighed in physical balance)

2 Sample made: 5 minutes (un-dry) and 30 minutes (dry)

POPC surfactant + NaI salt standardized in FA:

POPC at 5 times cmc = 0.3 m mol/g

NaI at 10^{-1} concentration

Mol. Wt. of POPC = 760 g/mol

Volume of FA = 80 ml

Amount of Substance = 10.332 mg (Mass of POPC from calculation)

Amount of Substance = 10.4 mg (Mass of POPC weighed in physical balance)

Amount of Substance = 0.00067 mg (Mass of NaI salt from calculation)

Amount of Substance = 0.00068 mg (Mass of NaI salt weighed in physical balance)

Sample made: 5 min. (un-dry with NaI salt)

Metastable Impact Electron Spectroscopy:

MIES has an exquisite surface sensitivity due to the fact that the energy carried by the object is used to excite the target electrons but the metastable He atom in its excited state cannot penetrate the analyte material so it releases its energy to the surface at a distance of a few Å [A]. Thus in a

MIES experiment, the surface sensitivity does not originate from the mean free path of the emitted electrons but from the fact that only electrons in the outermost layer can be excited. Therefore, MIES targets on the composition of that particular region which is important for interactions and reactions at surfaces or interfaces. MIES spectra are evaluated quantitatively [9, 10].

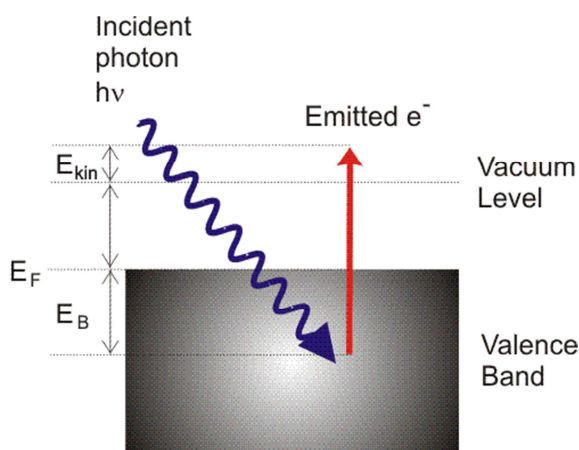


Figure 1. UPS Experimental Procedure.

Ultraviolet Photoelectron Spectroscopy:

UPS is a process in which the photon interacts with the valence levels of the molecule or solid thus by which DOS (density of states) occupied near the surface of the material is probed leading to ionization by removal of one of these valence electrons. In this technique, high voltage is applied to a gas to cause breakdown and UV photons of energy $h\nu$ are created in a continuous discharge source. These photons are then targeted onto the sample that undergoes analysis. These photons will liberate electrons with sufficient energy, from the sample and into the vacuum where their kinetic energies

may be analyzed to gain an idea of their energy origin in the density of states [11].

4. Results

4.1. UPS and MIES Spectra Comparison of POPC Surfactant Film on Si Surface at 3 Different Drainage States

Figure 2 presents an energy spectrum of the POPC surfactant film transferred on a silicon substrate in a non drained state i.e. transferred exactly in 5 minutes time after the bubble is formed, not giving the bubble enough time to drain the entire water layer from its core.

Likewise, Figure 3 presents the energy spectra of drained film i.e. film transferred in 30 minutes after the bubble formation, giving the bubble enough time to drain itself

Finally, Figure 4 presents the energy spectra of non drained POPC film with 10^{-1} mol/kg of NaI salt. In all the figures the energy spectra achieved both by UPS and MIES are presented.

The difference in the UPS spectrum and MIES spectrum can be observed clearly and even though both these techniques are chemically sensitive, MIES spectrum happens to be showing more information about the molecular orbitals of the outermost layer of the bilayer film than the UPS spectrum. The peak witnessed at 11.5 eV in the MIES spectra confirms the presence of POPC surfactant, whereas in the UPS spectra no specific reference towards the presence of POPC is observed. This could be due to the fact that the newly occupied state is present in the surface region and it does not seem to show much influence in the near surface region.

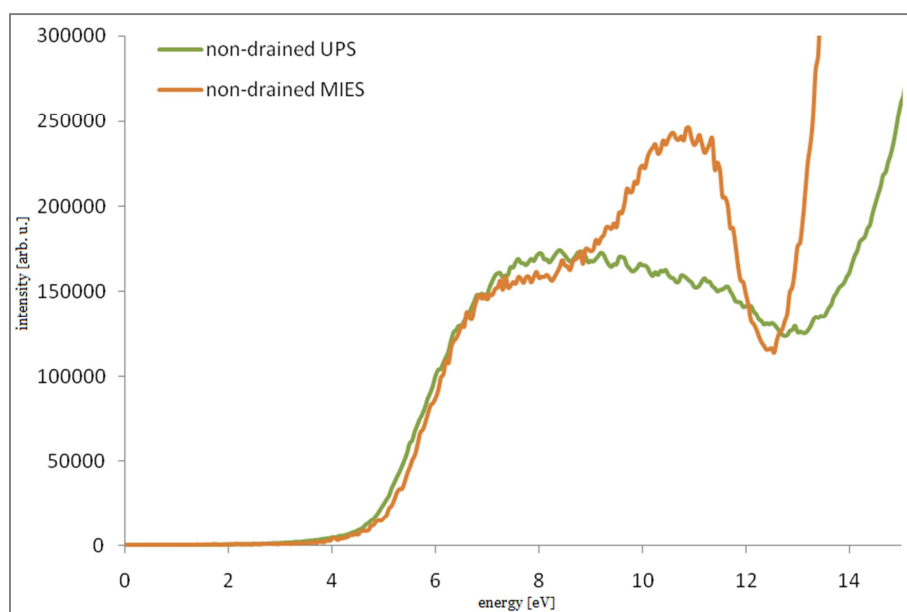


Figure 2. Energy Spectra of Non dried films.

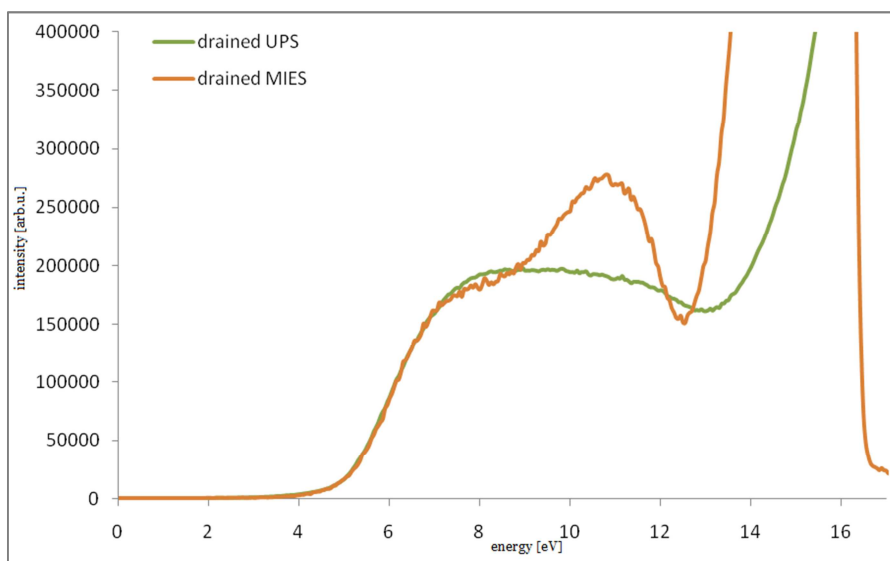


Figure 3. Energy Spectra of dried films.

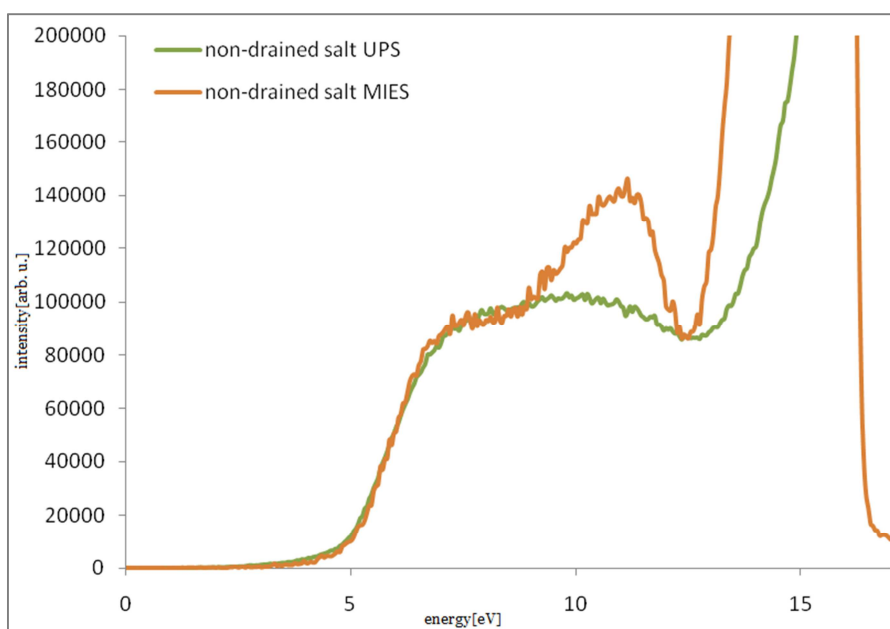


Figure 4. Energy Spectra of Dried film with NaI Salt.

4.2. Energy Spectra Comparison of POPC Surfactant Film on Si Surface in non Dried State (5 min), Dried State (30 min) and non Dried State with NaI Salt

Figure 5 presents the MIES spectra comparison of three different state of film and they differ in their drainage time and composition of the film. The spectra shows the fact that the non drained film records the high intensity than the drained film i.e. the absorbance unit of the non drained film is high compared to drained film but after the addition of a salt content like NaI, the film at the same drainage time shows different absorbance unit or very less absorbance unit.

The UPS spectrum shown in Figure 6 also agrees the same comparison at the beginning but they seem to differ later i.e. in the binding energy range of 6 – 12 eV the highest intensity is recorded for drained film and then the non drained film

and finally the non drained film with salt content. The reason could be due to the fact that, the newly occupied state concentrates mainly on the surface. However, in UPS the exciting radiation penetrates some distance into the sample, in order to determine the surface sensitivity by the mean free path of the emitted electrons. Thus, in UPS the signals from electrons are emitted from both the surface and the sub surface layer of up to few nanometers. So, the spectrum achieved from the sample could not be only due to change in surface structure. Whereas in MIES, the metastable atom carrying the energy required to excite the target electron is unable to penetrate the analyte material in its excited state, hence releases its energy to the surface at a distance of few Angstrom units. Thus, the surface sensitivity in MIES is achieved from the fact that the electron in the outermost layer can only be excited.

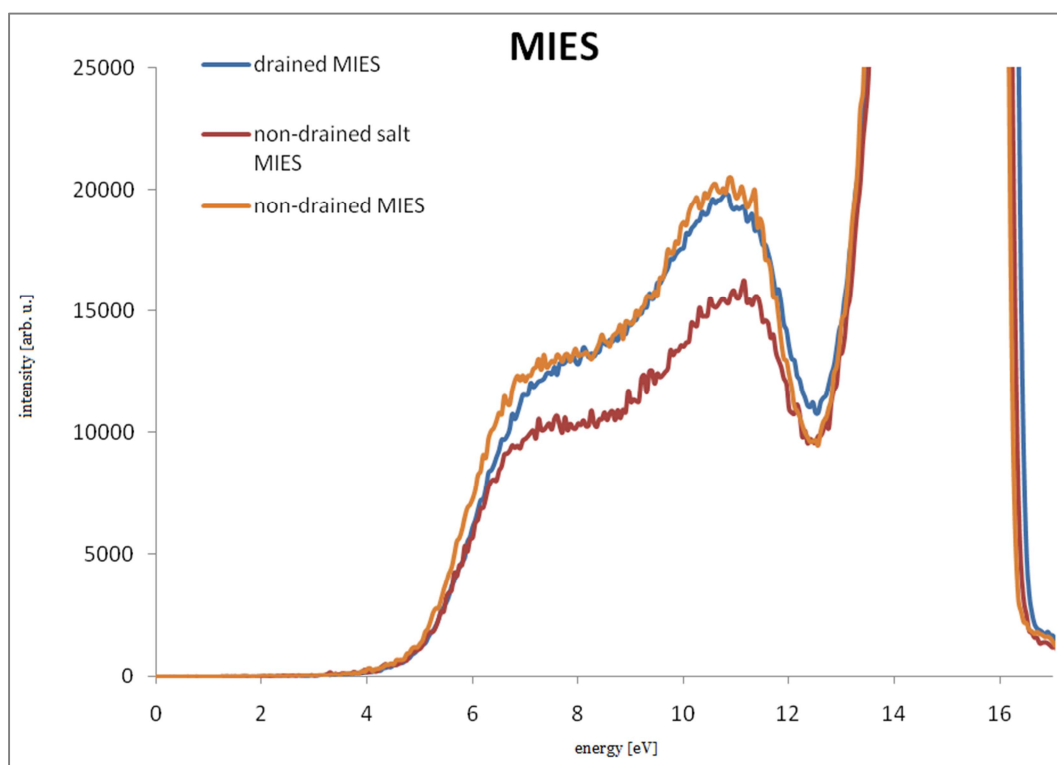


Figure 5. MIES spectra of 3 different transferred film.

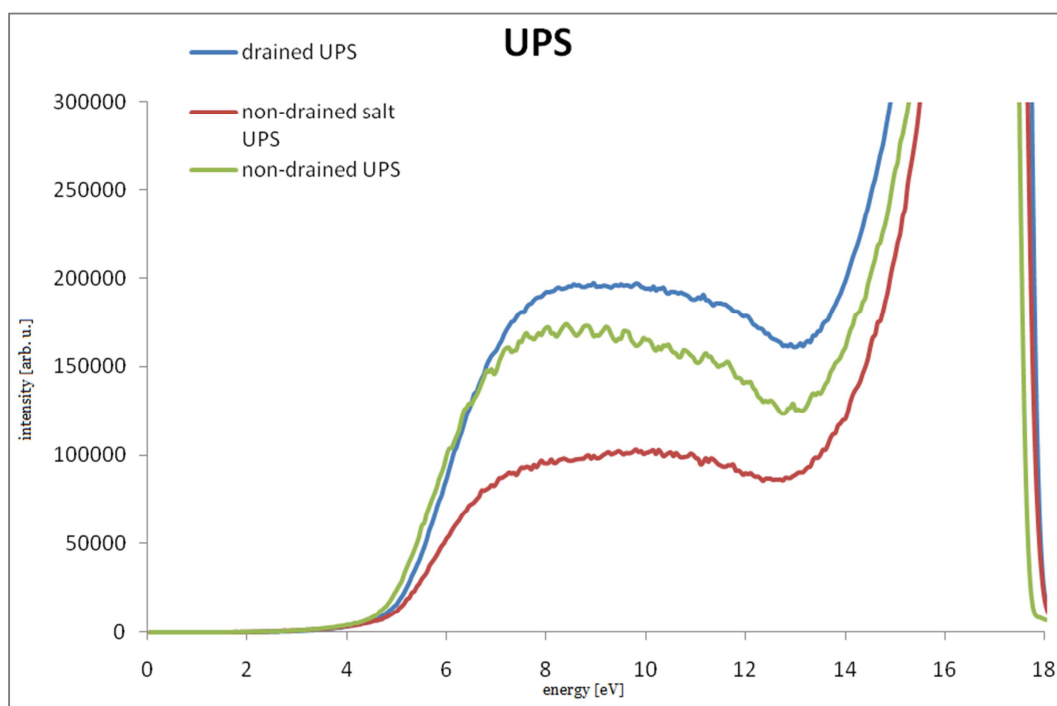


Figure 6. UPS spectra of 3 different transferred film.

5. Discussions

The above shown result proves the fact that MIES spectra seems to capture more detail about the outermost layer of the surfactant film regarding their structure and molecular

orientation than the UPS spectra. As mentioned in Figure 2,3 &4 the peak observed in MIES spectra shows the presence of an occupied state and information about their molecular orbitals that are exposed at the surface level and no such observation is witnessed in the UPS spectrum and thus the

discrepancy with the highest intensity recorded in both the spectra. As far the change in surface structure is concerned, the MIES peak formed at 7 eV could be due to the presence of non bonding state like O in the surfactant film and the peak formation at 11.5 eV could be due to the present of bonding state of Si-O. This information changes with UPS spectra as, even though the thickness of the film deposited is of the order of 10 nm and UPS are capable of providing information depth of about 50-60 nm at a Photoelectron kinetic energy of 21keV, it can only be helpful in monitoring the intensity due to the substrate density of states near the Fermi-edge but information regarding the change of structure is less adequate. So, comparatively MIES energy spectra happen to be the most eligible analysis towards the change in molecular orientation on the sample surface.

As far as the change in surface structure of the film is concerned MIES spectra seems to show more on the presence of new elements through the variation in spectra with the drainage time and also more information about their structure and molecular orientation. This is due to the fact that in an un-dried film the molecules forming the outermost layer have various orientations and the electrons of various orbital are witnessed in the spectrum. However, upon maximal drainage the films become more thinner and thus allowing the molecules in them to become patterned. This patterned film contains molecules that are of same orientation in their outermost layer and in the spectrum, only electrons of the orbital forming one side of the molecule is witnessed. Thus the gradual variation in the result confirms that the spectrum of the surface molecular structure gets well-defined with more ordered outermost layer.

This pattern structure could be achieved more quickly with the addition of a salt like NaI; this is due to the fact that the thickness of a Black film or Common Black Film is sensitive towards ionic strength and introducing a salt in the surfactant mixture varies the ionic strength on certain level. The film becomes thinner quickly thus forcing the outer most layer to form into a pattern.

6. Conclusions

Assembling nanomaterial over a solid surface is vital in order to render their electronic and optical properties; but handling nanoparticles and achieving a system with nanoscale arrangement is tough for obvious reasons. The most effective method is to insert these nanoparticles into a surfactant and allow them to form a film; this way the nanoparticles become ordered after the water in the film drains. Transferring this film onto a solid substrate preserves the structure and molecular orientation of the film even after deposition. The article illustrates that the molecules deposited make their impact predominately along the surface of the sample and arrange themselves along the outermost layer. Hence comparatively MIES spectra being surface sensitive show more confident results than UPS spectra. The formation of the peak in the three different states of drainage confirms that the structure becomes more ordered with time i.e. more

the film is allowed to drain before deposition the more the molecules becomes patterned. Thus, the MIES spectra of the drained substrate are predominant due to the fact that it is achieved through the excitation of molecules alone and does not involve any water layer. This process get even quicker with varying the Ionic strength through addition of salt like Sodium Iodide.

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