Lecture-11

Superlattices, Self Assembly & LB Films

Two-Dimensional Nanostructures Cont…

(Ref: Guozhong Cao;
Nanostructures & Nanomaterial: Synthesis, Properties & Applications)

Super Lattices

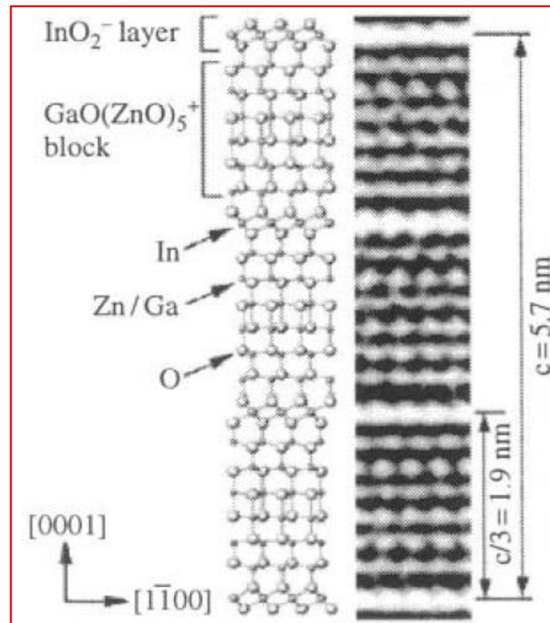
- Structures composed of periodically alternating single crystal film layers.
- When both layers are relatively thick, properties of bulk materials are observed due to the frequently synergistic extensions of the laws of property mixtures that are operative.
- However, when the layers are very thin, quantum effects emerge, since the wavefunctions of charge carriers in adjacent thin layers penetrate the barriers and couple with one another.
- Such structures are mostly fabricated by MBE; however, CVD methods are also capable of making superlattices.

- ALD is another unique technique in the fabrication of superlattice structures.
- Semiconductor superlattices can be categorized into compositional superlattices and modulation doping, i.e. selective periodic doping, superlattice.
- The fabrication of semiconductor superlattices is basically the controlled synthesis of band gap structures, which is also known as band gap engineering.

Some examples of super lattice system

Film materials	*Lattice mismatch*	*Deposition methods*
GaAs–$As_xGa_{1-x}As$	0.16% for x = 1	MBE, MOCVD
$In_{1-x}Ga_xAs$–$GaSb_{1-y}As_y$	0.61%	MBE
GaSb–AlSb	0.66%	MBE
InP–$Ga_xIn_{1-x}As_yP_{1-y}$		MBE
InP–$In_{1-x}Ga_xAs$	0%, x = 0.47	MBE, MOCVD, LPE
GaP–$GaP_{1-x}As_x$	1.86%	MOCVD
GaAs–$GaAs_{1-x}P_x$	1.79%, x = 0.5	MOCVD, CVD
Ge–GaAs	0.08%	MBE
Si–$Si_{1-x}Ge_x$	0.92%, x = 0.22	MBE, CVD
CdTe–HgTe	0.74%	MBE
MnSe–ZnSe	4.7%	MBE
PbTe–$Pb_{1-x}Sn_xTe$	0.44%, x = 0.2	CVD

Superlattice crystal structure of $InGaO_3(ZnO)_5$



Self-Assembly

- Self-assembly is a generic term used to describe a process that ordered arrangement of molecules and small components such as small particles occurred spontaneously under the influence of certain forces such as chemical reactions, electrostatic attraction and capillary forces.
- We will focus our discussion on the formation of monolayer or multiple layers of molecules through self-assembly.
- In general, chemical bonds are formed between the assembled molecules & the substrate surface, as well as between molecules in the adjacent layers.

- Therefore, the major driving force is the reduction of overall chemical potential.
- A variety of interactions or forces have been explored as driving forces for the self-assembly of nanometer as the fundamental building blocks.
- The driving force for the self-assembly includes: electrostatic force, hydrophobicity and hydrophilicity, capillary force and chemisorption.
- There are several types of self-assembly methods for the organic monolayers and these include (i) organosilicon on hydroxylated surfaces, such as SiO_2 on Si, Al_2O_3 on Al, glass, etc. (ii) alkanethiols on gold, silver and copper. (iii) dialkyl sulfides on gold. (iv) dialkyl disulfides on gold (v) alcohols and amines on platinum, and (vi) carboxylic acids on aluminum oxide and silver.

- Another way to group the self-assembly methods could be based on the types of chemical bonds formed between the head groups and substrates.
- Three different ways are mentioned below:

    (i) Covalent Si-0 bond between organosilicon on hydroxylated substrates that include metals and oxides,

    (ii) Polar covalent S-Me bond between alkanethiols, sulfides and noble metals such as gold, silver, platinum and copper, and

    (iii) Ionic bond between carboxylic acids, amines, alcohols on metal or ionic compound substrates.

Langmuir-Blodgett Films

- Langmuir-Blodgett films (LB films) are monolayers and multilayers of amphiphilic molecules transferred from the liquid-gas interface (commonly water-air interface) onto a solid substrate and the process is generally referred to as Langmuir-Blodgett technique (LB technique).
- Langmuir carried out the first systematic study on monolayers of amphiphilic molecules at the water-air interface and the first study on a deposition of multilayers of long-chain carboxylic acid onto a solid substrate was carried out.

- The amphiphile is a molecule that is insoluble in water, with one end that is hydrophilic, preferentially immersed in the water and the other that is hydrophobic, preferentially resides in the air or in the nonpolar solvent.
- A classical example of an amphiphile is stearic acid, $C_{17}H_{35}COOH$.
- In this molecule, the long hydrocarbon tail, $C_{17}H_{35}$ - is hydrophobic, and the carboxylic acid head group, -COOH is hydrophilic.
- Since the amphiphiles have one end that is hydrophilic and the other that is hydrophobic, they like to locate in interfaces such as between air and water, or between oil and water.
- This is the reason they are also called surfactants.

- The solubility of an amphiphilic molecule in water depends on the balance between the alkyl chain length and the strength of its hydrophilic head.
- Certain strength of the hydrophilic head is required to form LB films.
- If the hydrophilicity is too weak, no LB film can be formed.
- However, if the strength of the hydrophilic head is too strong, the amphiphilic molecule is too soluble in water to allow the formation of a monolayer.
- Table summarizes the properties of different head groups.
- The soluble amphiphile molecules may form micelles in water when their concentration exceeds their critical micellar concentration.

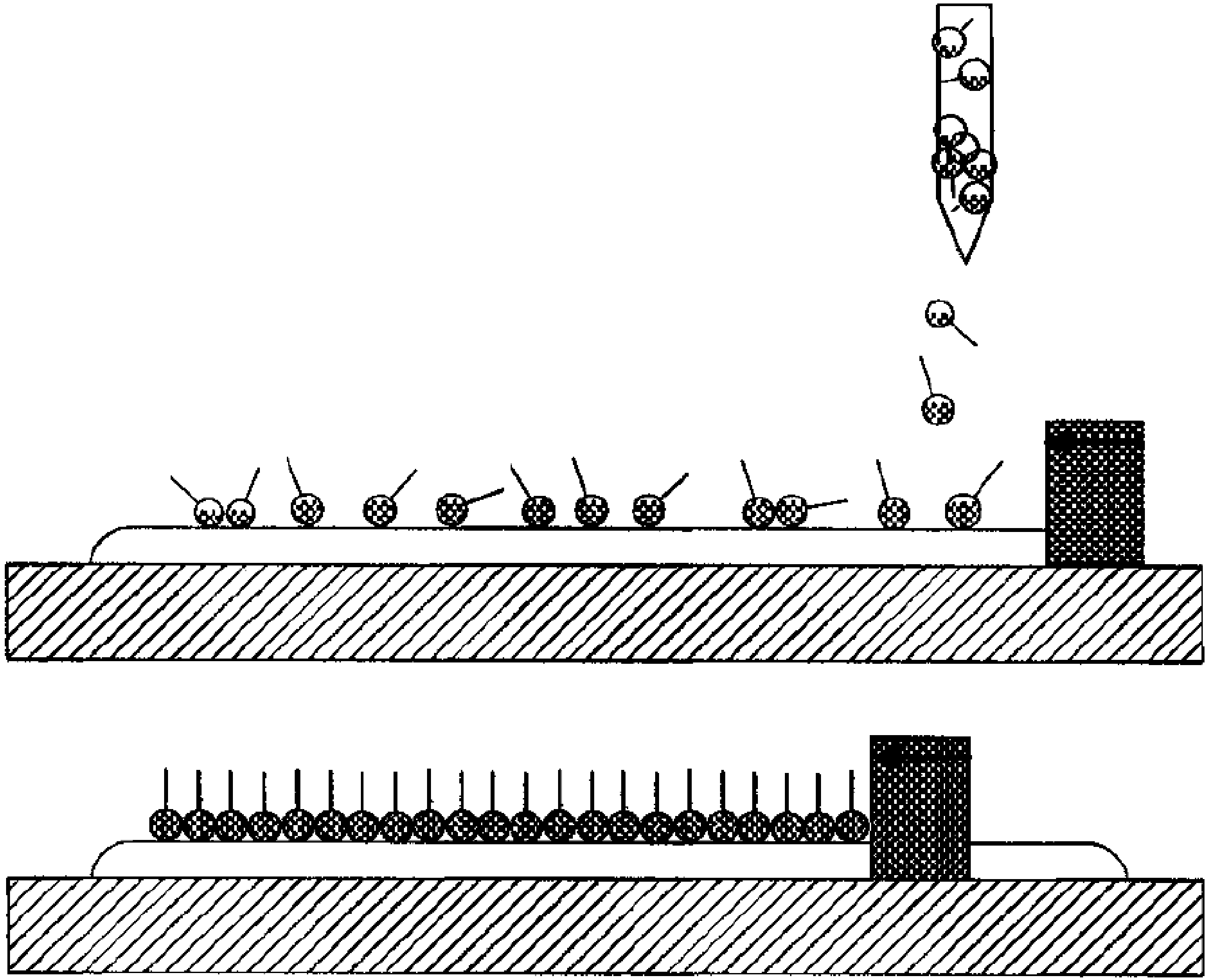
The effect of different functional groups on LB film formation of C_{16}-compounds

Very weak (no film)	*Weak (unstable film)*	*Strong (stable LB film)*	*Very strong (soluble)*
Hydrocarbon	$-CH_2OCH_3$	$-CH_2OH$	$-SO_3^-$
$-CH_2I$	$-C_6H_4OCH_3$	$-COOH$	$-OSO_3^-$
$-CH_2Br$	$-COOCH_3$	$-CN$	$-C_6H_4SO_4^-$
$-CH_2Cl$		$-CONH_2$	$-NR_4^+$
$-NO_2$		$-CH{=}NOH$	
		$-C_6H_4OH$	
		$-CH_2COCH_3$	
		$-NHCONH_2$	
		$-NHCOCH_3$	

- The LB technique is unique, since monolayers can be transferred to many different substrates.
- Most LB depositions have involved hydrophilic substrates where the monolayers are transferred in the retraction mode.
- Glass, quartz and other metal substrates with an oxidized surface are used as substrate, but silicon wafer with a surface of silicon dioxide is the most commonly used substrate.

- Gold is an oxide-free substrate and also commonly used to deposit LB films.
- However, gold has a high surface energy (~ 1000 mJ/m^2) and is easily contaminated, which results in an uneven quality of LB films.
- Cleanliness of the substrate surface is crucial to high quality LB films.
- In addition, the purity of the organic amphiphiles under study is of great importance, since any contamination in the amphiphile will be incorporated into the monolayer.

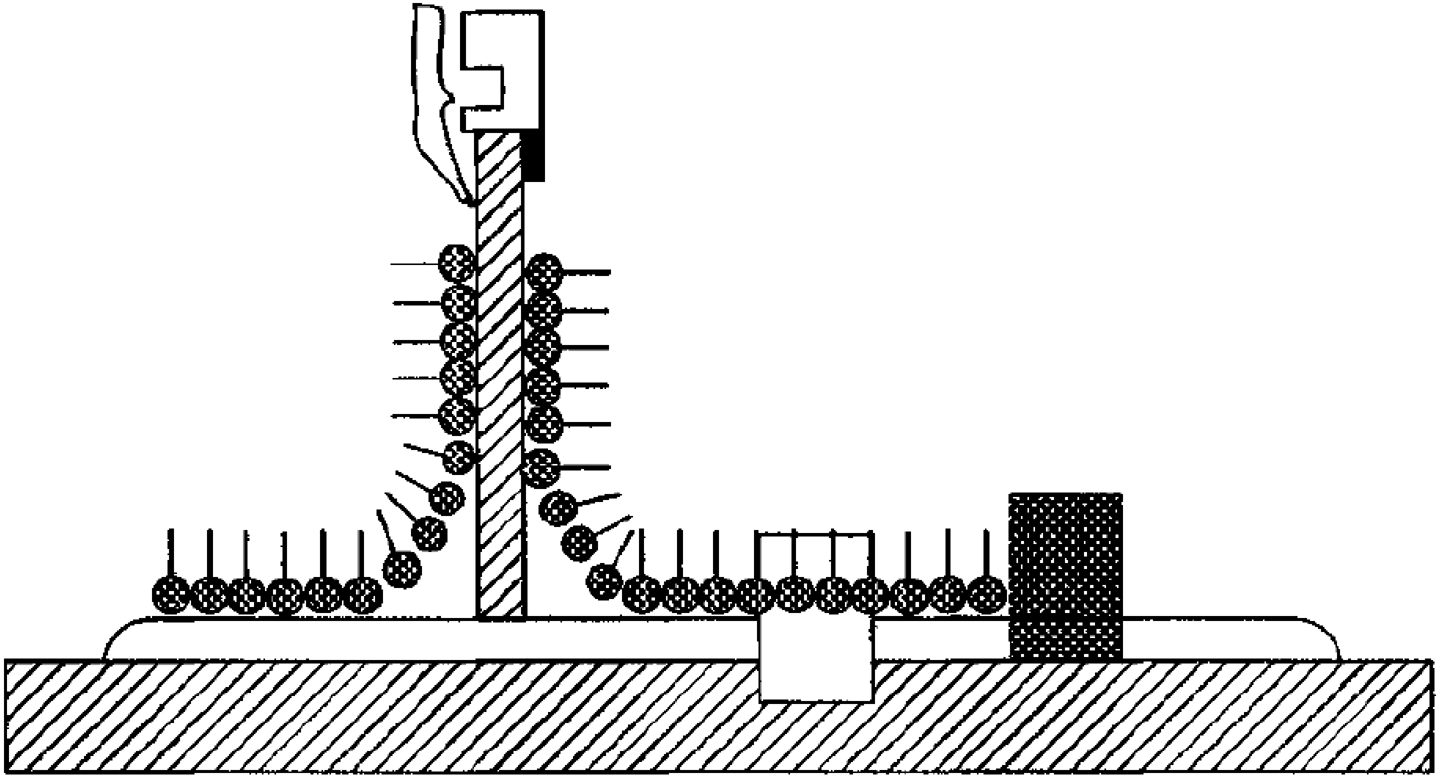
- Figure schematically shows the formation of Langmuir films, which denote the molecular films at the water-air interface.
- A drop of a dilute solution of an amphiphilic molecule in a volatile solvent, such as $CHCl_3$, is spread on the water-air interface of a trough.
- As the solvent evaporates, amphiphilic molecules are dispersed on the interface.
- The barrier moves and compresses the molecules on the water-air interface; the intermolecular distance decreases and the surface pressure increases.



Schematic showing the formation of Langmuir films, which denote the molecular films at the water-air interface, a drop of a dilute solution of an amphiphilic molecule in a volatile solvent, such as $CHCl_3$, is spread on the water-air interface of a trough.

- A phase transition may occur, which is assigned to a transition from the “gas” to the “liquid” state.
- In the liquid state, the monolayer is coherent, except the molecules occupy a larger area than in the condensed phase.
- When the barrier compresses the film further, a second phase transition can be observed from the “liquid” to the “solid” state.
- In this condensed phase, the molecules are closely packed and uniformly oriented.

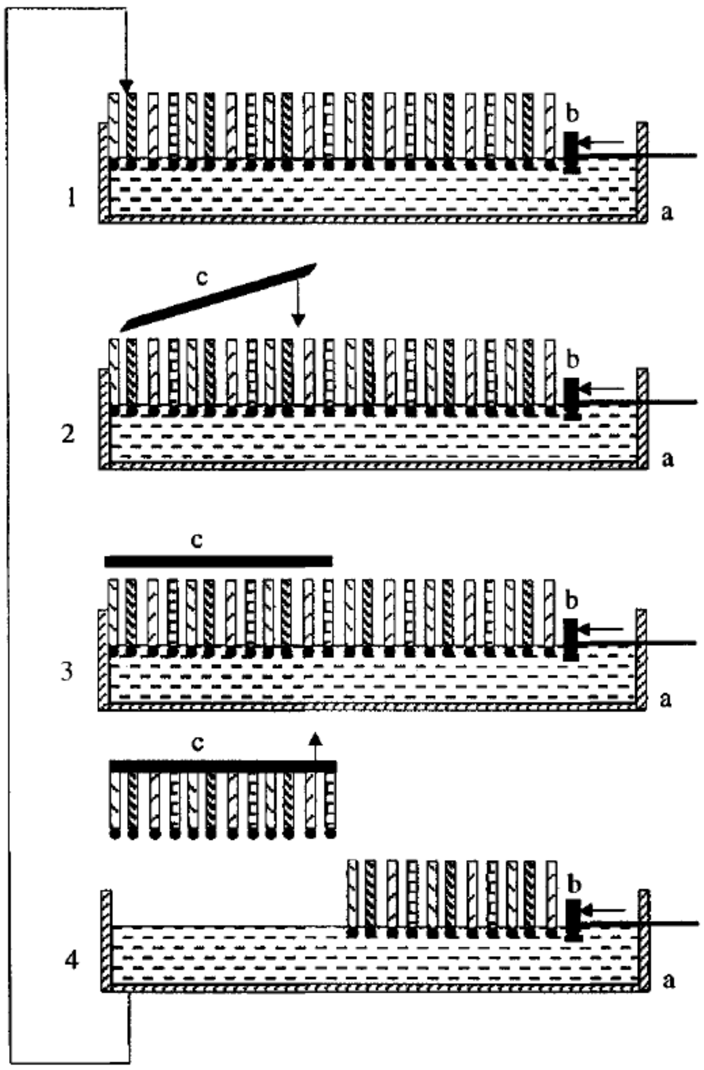
- Two methods are commonly used to transfer monolayers from the water-air interface onto a solid substrate.
- The more conventional method is the vertical deposition as sketched below:



The more conventional vertical deposition method for the formation of LB films on substrates.

- When a substrate is moved through the monolayer at the water-air interface, the monolayer can be transferred during emersion (retraction or upstroke) or immersion (dipping or down stroke).
- A monolayer usually will be transferred during retraction when the substrate surface is hydrophilic, and the hydrophilic head groups interact with the surface.
- However, if the substrate surface is hydrophobic, the monolayer will be transferred in the immersion, & hydrophobic alkyl chains interact with the surface.
- If the deposition process starts with a hydrophilic substrate, it becomes hydrophobic after the first monolayer transfer, and thus the second monolayer will be transferred in the immersion.
- Multiple layer films can be synthesized just by repeating the process.

- Another method to build LB multilayer structure is the horizontal lifting, also referred to as Schaefer's method.
- Schaefer's method is useful for the deposition of very rigid films.
- In this method as shown in Fig., a compressed monolayer is first formed at the water and air interface.
- A flat substrate is placed horizontally on the monolayer film.



Schaefer's method useful for the deposition of very rigid films, in which, a compressed monolayer is first formed at the water and air interface, a flat substrate is placed horizontally on the monolayer film.

- When the substrate is lifted and separated from the water surface, the monolayer is transferred onto the substrate.
- Thermal stability and order-disorder transition are two important issues for any practical applications of LB films.
- Although a lot of research has been done in the past two decades, many issues remain unsolved and our understanding on the structures and stability of LB films is still very limited.

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