Department of Materials Science and Engineering
Norwegian University of Science and Technology

TMT4320 Nanomaterials, fall 2015

EXERCISE 11 - SOLUTION

PROBLEM 1

a) *Langmuir-Blodgett film formation* (wet-chemical deposition method)

Monolayers and multilayers of amphiphilic molecules (surfactants) are transferred from the liquid-gas interface (commonly water-air) interface onto a solid substrate. The process is generally referred to as Langmuir-Blodgett technique. Monolayers can be transferred to many different substrates. Most LB depositions have involved hydrophilic substrates where the monolayers are transferred in the retraction mode (SiO_2-coated Si, glass/quartz, metal substrates with oxidized surfaces).

b) *Spin coating* (wet-chemical deposition method)

Spin coating is a procedure used to apply uniform thin films to flat substrates. An excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid to, and eventually off, the edge of the substrate by centrifugal force. The film thickness can be controlled by adjusting the solution/dispersion properties and the deposition conditions (rotation speed, sol viscosity, wetting properties).

c) *Molecular beam epitaxy* (MBE) (physical vapor deposition method):

MBE can be considered as special case of evaporation for high-quality film growth. The molecular beam(s) is generated by heating the source (solid material) to desired temperature using resistive heating in an effusion cell (Knudsen cell). An MBE system typically consists of several effusion cells with different precursor materials (metals). The molecular beam from each effusion cell is controlled by a shutter in front of the effusion cell. In the reaction chamber the vacuum is ultrahigh: $\sim 10^{-10}$ torr. The evaporated atoms or molecules do not interact with each other in the vapor phase due to the low pressure. The main attributes of MBE are the extremely clean environment, low growth temperature, slow growth rate (typically 1 μm/h), simple growth mechanism (better understanding of process due to ability to individually control evaporation of sources), and a variety of *in situ* analysis capabilities which give better understanding and ability to refine the process.

d) *Pulsed laser deposition* (PLD) (physical vapor deposition method):

Pulsed laser deposition is a technique where a high power, pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This material is vaporized from the target (in a plasma plume) which deposits it as a thin film on a substrate. This process can occur in ultrahigh vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films.

To synthesize multilayers, the targets are placed successively in the beam and rotated to avoid local damage. Several parameters can be exploited to control the film growth: the substrate temperature, the substrate–target distance, and the residual pressure in the chamber, together with the intrinsic characteristics of the laser beam. An important advantage of PLD is that the material is transferred stoichiometrically from the target to the substrate. This facilitates deposition of multi-element materials such as oxides (Al_2O_3, SiO_2, YBCO, etc.). There is thus a wide choice of materials that can be deposited, limited only by absorption at the laser wavelength.

e) *Magnetron sputtering* (physical vapor deposition method):
[Since a SmCo magnet (or more correct several magnets constituting a magnetron) is located beneath the target, the method is not pure cathodic sputtering.]

In general, sputtering is a process whereby atoms are ejected from a solid target material due to bombardment of the target by ions with high enough energy (> 30 eV). This surface erosion phenomenon, leading to the formation of an atomic vapor, results from elastic collisions with energy and momentum transfer between the incident ions and the target atoms. The ions (plasma) are produced in a chamber into which an inert gas is introduced (usually argon) at low pressure by applying a potential difference of kV order between the substrate holder (anode) and the target (cathode).

In magnetron sputtering, a special magnetic device is associated with the cathode to confine electrons close to the target surface and thereby increase the plasma density, and hence the sputtering rate. The cathode, or magnetron target, is equipped with permanent magnets arranged behind the target and which produce a strong magnetic field with closed field lines. The secondary electrons emitted by the cathode under the effect of ion bombardment of the target surface are trapped and follow trajectories that spiral along the field lines. There is increased probability that these electrons will ionize argon atoms. The high ion density means that the discharge can be maintained at lower pressure (up to 10^{-2} Pa) compared to pure cathodic sputtering. Another important parameter is the ion energy, and hence the energy of the atoms deposited on the substrate, which is higher in the magnetron sputtering process. This plays a key role in the growth of the films, which are denser and adhere better.

When the aim is to form metal nitrides or oxides by reactive magnetron sputtering, a reactive gas must be added to the main gas (argon), but radio-frequency (RF) mode must be used and the pressure of the reactive gas must be controlled. In RF mode, the sign of the anode-cathode bias is varied at a high rate and charge build-up on insulating targets can then be avoided.

f) *Electrophoretic deposition* (wet-chemical deposition method):
[NB: not sputtering as there is growth from a suspension]

Charged colloidal particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in electrophoretic deposition. This includes materials such as polymers, pigments, dyes, ceramics and metals. The process is useful for applying materials to any electrically conductive surface. Aqueous EPD is the most common commercially used EPD process, however, non-aqueous electrophoretic deposition applications are known.

PROBLEM 2

a) Molecular beam epitaxy (MBE) is probably the best choice. Vapor-phase deposition methods are necessary; such materials are challening to obtain by liquid-phase methods. III-V semiconductor materials are often grown by MBE. The growth of nitrogen- and phosphor-containing III-V materials is possible by MBE. Another method, metalorganic chemical vapor deposition (MOCVD), might be even better suited in this case. However, that method has not been covered in this course, and would not be expected for this answer.

b) Self-assembled monolayer formation, by immersing the gold substrate in a solution containing hexadecanethiol molecules. The molecules will self-assemble into a monolayer on the gold substrate because of the strong chemisorption of the thiol group onto the gold surface. The method is cheap and easy, but takes some hours to complete.

c) Radio-frequency magnetron sputtering and pulsed laser deposition (PLD) are probably the two methods that are most used. Several other methods can be used: chemical solution deposition (dip/spin coating) of very low concentration precursor solutions, metalorganic CVD, and possibly molecular beam epitaxy (MBE). The advantages of RF magnetron sputtering and PLD compared to the other methods are that they do not require subsequent annealing, no toxic gases are used or produced, a single target can be used, the pressure inside the chamber is higher than for MBE (and thereby easier to achieve and maintain), and the methods are relatively fast.