

## Solutions for PHYS6014

### A questions:

**A1. Conventional photolithography is reaching its limit in the fabrication of integrated circuits. Explain what this limit is and why it exists and name two other “top-down” nanofabrication methods.**

The widths of the finest lines that can be put on a chip in optical lithography are limited by optical diffraction. The light that exposes the photoresist comes through an aperture defined by the metal walls of the mask and the sharpness of the image of the mask on the photoresist is limited by the wavelength of the light. [1 mark]

At present this limits lines to being at least 22 nm. [1mark]

Acceptable answers for top-down nanofabrication methods include:

e-beam lithography and micro-contact printing, dip-pen-lithography [2 marks]

**A2. Define the tunnelling current ( $I_t$ ) that can be measured in scanning tunnelling microscopy, stating all the terms in this definition. Why is the spatial resolution of the STM better than the AFM ?**

$$I \propto \int_{E_f - eV_b}^{E_f} |Y_n(0)|^2 \exp(-2ad)$$

where  $d$  = tip-sample spacing;  $\alpha$  = decay constant of wavefunction,  $|\Psi|^2$  = amplitude of the wavefunction. [1 mark correct formula, 1 mark correct definitions]

The higher resolution of the STM comes from the fact that overlap of atomic wave functions, which are exponentially decaying in space, are the means of detection. The decay of the wave function may be localized on the scale of the Bohr radius, 0.053 nm. If a tip is made of atoms, it may turn out that only one atom contributes appreciably to the current, and this is the origin of the atomic resolution. The AFM senses the van der Waals force, which has a slower decay in space, and for this reason the sensing of the force is spread out over a larger region, a large number of atoms, and the spatial resolution is diminished. [2 marks]

**A3. (i) Give two reasons to justify that surface-enhanced Raman scattering is an intrinsically nanoscale phenomena.**

- It occurs only when metallic nanomaterials are used.
  - The electric fields which are responsible for surface enhanced Raman are generated at the nanoscale
  - The electric fields exploited in surface-enhanced Raman have nanoscale decay lengths
  - The plasmons are generated by nanoparticles
  - Surface plasmon resonances occur at nanoscale dimensions in metallic materials
- [2 marks]

**(ii) What is surface plasmon resonance? What will happen to the surface plasmon resonance peak with increasing size in spherical gold or silver nanoparticles?**

The collective oscillation of electrons on the surface of a metallic material (or any material with free/conduction electrons) coupled to electromagnetic radiation is known as surface plasmon resonance. [1 mark]

The surface plasmon resonance peak red-shifts with an increase in size of spherical nanoparticles of gold or silver. [1 mark]

**A4. Explain the electrostatic and steric surface stabilisation of colloidal inorganic nanoparticles. Name and explain the two types of interactions between the ligand and the surface of the nanoparticle. What are the advantages of steric stabilisation against electrostatic stabilisation ? (Assume that sterically stabilised particles are fully covered with ligands).**

Electrostatic stabilization is due to mobile ions that surround the surface of nanocrystals. The nanocrystals are prevented from aggregation due to the electrostatic repulsion and/or osmotic flow. Steric stabilisation is due to the presence of ligands on the surface of the nanoparticles. The repulsion in this case is due to a volume restriction effect arising from the decrease in possible configurations in the region between the two surfaces and/or due to an osmotic effect because of the relatively high concentration of adsorbed molecules in the region between the two particles. [1 mark]

The two types of steric interactions are a) Chemisorption where an anchored ligand is covalently binds to the surface of the nanoparticle (i.e a thiol –gold bond or a amine-silver bond), and b) adsorption where the ligand is adsorbed at the surface of the nanocrystal (i.e. due to hydrophobic, van der Waals interactions). [1 Mark]

Four are the basic advantages of steric to electrostatic stabilization : a) Particles with a high coverage of ligands are always re-dispersible, b) very high concentration of particles can be accommodated in a solution c) particles are not electrolyte sensitive and d) particles can be well- dissolved in different solvents by appropriate choice of the stabilizer. [2 marks]

**A5. What is the bottom-up synthetic approach? What drives this approach? Name three synthetic methods where the bottom-up approach is employed.**

At the bottom up synthetic approach ionic, atomic or molecular units are assembled through various processes to form structures larger structures. This approach includes small units that come together in an organized (bottom up) approach. This approach is driven mainly by the reduction of Gibbs free energy. To have  $\Delta G$  as negative as possible,  $\Delta H$  should get small and  $\Delta S$  large.  $\Delta H$  is related to the surface energy and  $\Delta S$  is related to the objects and the space that they occupy. [2 marks]

Some examples of the bottom up approach are gas phase methods (e.g. chemical vapour deposition), non-biological liquid phase methods (e.g. reduction of metal salts), bottom-up lithographic methods (e.g. STM writing), biological and inorganic methods (e.g. formation of DNA of sugars, phosphate and nucleosides). [2 marks]

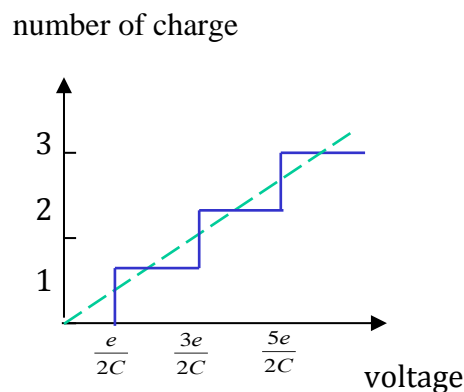
**B questions:**

**B1.**

**(i) Describe the Coulomb blockade effect and Coulomb staircase in a single electron transistor with the aid of a diagram that shows the charge vs. voltage behaviour**

(i) In a single-electron transistor, the charging energy associated with electron tunnelling becomes a potential barrier for electron transfer. This effect is known as the *Coulomb blockade*. [3 marks]

The critical voltage across the transistor needed to transfer an electron onto the island, equal to  $e/C$  [1 mark], is called the Coulomb gap voltage [1 mark]. *Coulomb staircase* refers to the step-wise characteristics shown in the number of charges measured when increasing the voltage [1 mark].



For sketch [4 marks]

**(ii) Consider the conducting islands isolated in a single electron transistor. For the transistor to work at room temperature, what should the capacitance of the island be? If the island can be modelled as a sphere, calculate its radius.**

(ii) If at RT,  $kT \sim 25 \text{ meV} = 0.025 \text{ eV}$

$$\text{charging energy } U = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} \frac{e^2}{C} [\text{in } J] = \frac{1}{2} \frac{e}{C} [\text{in } eV]$$

When  $U > kT$ , the Coulomb blockade effect can be measured.

$$\frac{1}{2} \frac{e}{C} > 0.025, \quad C < \frac{1}{2} \frac{e}{0.025} = \frac{1.6 \cdot 10^{-19}}{0.05} = 3.2 \cdot 10^{-18} [F]$$

[4marks]

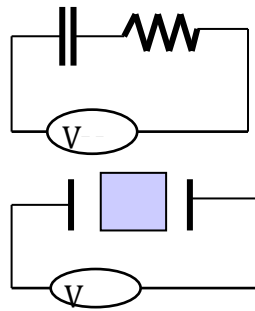
Assume the island is a sphere with radius of  $r$

$$C = 4\pi\epsilon_0\epsilon_r, \quad r = \frac{C}{4\pi\epsilon_0} = \frac{3.2 \times 10^{-18}}{4 \times 3.14 \times 1 \times 8.854 \times 10^{-12}} = 2.9 \times 10^{-8} \text{ m} = 29 \text{ nm}$$

[2 marks].

**(iii) Sketch and explain the difference between charging up a capacitor via classical polarization and via a quantum tunneling process.**

The difference between the classical capacitor charging and quantum tunnelling is that the former does not involve quantized charge transfer, but only displacement or polarization charge which could be infinitely small. The latter involves transferring of individual electrons, hence change of charge by integer of electron charge [2 marks]



[2 marks] for the sketch or sketch expressed in words.

## B2a.

**(a) Scanning probe microscopies are invaluable tools for the nanoscale characterization of surfaces and structures. (i) State whether for semiconductor surfaces the STM images acquired depend on the polarity of the bias voltage and justify your answer. (ii) In the simplest limit an STM image represents contours of constant tunnelling current. Under what conditions does this simple limit break down? Name two reasons. (iii) The following constant-current STM images were acquired on the GaAs (110) surface at a bias voltage of +1.9 V (left-hand image) and -1.9 V (right-hand image). What can be observed in the images at different bias voltages and why.**

(i) The STM image of a semiconductor obtained with plus or minus bias voltages differs. [2 marks]

For a semiconductor the top portion of the VB (involved in surface-to-tip tunneling) usually differs from the bottom portion of the CB (involved in tip-to-surface tunneling) in orbital character. [2 marks]

(ii) This simple correlation between the tunneling current and topography breaks down when adsorbed species are present [1mark], or the sample is a semiconductor [1 mark]

(iii) Maxima observed at positive biases correspond to Ga sites and at negative biases to As sites [1 mark].

Charge transfer occurs from Ga to As atoms, leaving the Ga dangling bond more empty and the As dangling bond more full. Occupied state density concentrates around the As while unoccupied state density is concentrated around the Ga. [1 mark]

## B2b.

**(i) What is self-assembly? What are the principles of molecular self-assembly? Name two self-assembly interactions that are taking place between two DNA strands.**

(i) Self-assembly is a process in which components, either separate or linked, spontaneously form ordered aggregates. Self-assembly can occur with components having sizes from the molecular to the macroscopic, provided that appropriate conditions are met. [1 Mark]

The principles of molecular self-assembly are :

**Components:** A self-assembling system consists of a group of molecules or segments of a macromolecule that interact with one another.

**Interactions:** Self-assembly occurs when molecules interact with one another through a balance of attractive and repulsive interactions. These interactions are generally weak (that is, comparable to thermal energies) and non-covalent.

**Reversibility (or Adjustability):** For self-assembly to generate ordered structures, the association either must be reversible or must allow the components to adjust their positions within an aggregate once it has formed.

**Environment:** The self-assembly of molecules normally is carried out in solution or at an interface to allow the required motion of the components. [4 Marks]

An example of a self-assembly process is the interaction between two DNA strands. Two DNA strands assemble together by a) creating hydrogen bonds between base pairs (AT two

hydrogen bonds and GC three hydrogen bonds) and b)  $\pi$ - stacking between the aromatic compounds. [1 Mark]

(ii) Assume a spherical nanoparticle nucleus with a radius of  $r$ . The total change of the Gibbs' free energy for the formation of the nucleus ( $\Delta G_{nuc}$ ) is given by:

$$\Delta G_{nuc} = \Delta G_v \frac{4}{3} \pi r_{nuc}^3 + \gamma 4\pi r_{nuc}^2$$

$\Delta G_{nuc}$  = change of Gibbs free energy

$\Delta G_v$  = change of volume free energy

$\gamma$  = surface energy per unit area

The nucleus will be stable only when its radius exceeds a critical size,  $r^*$ . Show that critical size,  $r^*$ , and critical energy ( $\Delta G^*$ ) are given by:

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad \Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2}$$

At the critical size:

$$\frac{\partial \Delta G_{nuc}}{\partial r} \Big|_{r=r^*} = 0$$

Knowing that:

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (1)$$

$$r = r^* \Rightarrow \frac{d\Delta G}{dr} = 0$$

the derivative of (1) is:

$$\frac{d\Delta G}{dr} = \frac{4}{3} 3\pi r^2 \Delta G_v + 4 \times 2\pi r \gamma = 4\pi r^2 \Delta G_v + 8\pi r \gamma = 0 \Leftrightarrow$$

$$r^*(4\pi r^2 \Delta G_v + 8\pi r \gamma) = 0 \Leftrightarrow r^* = 0 \vee r^* = -2 \frac{\gamma}{\Delta G_v}$$

and thus the critical radius is:

$$r^* = -2 \frac{\gamma}{\Delta G_v} \quad (2)$$

**[3 Marks]**

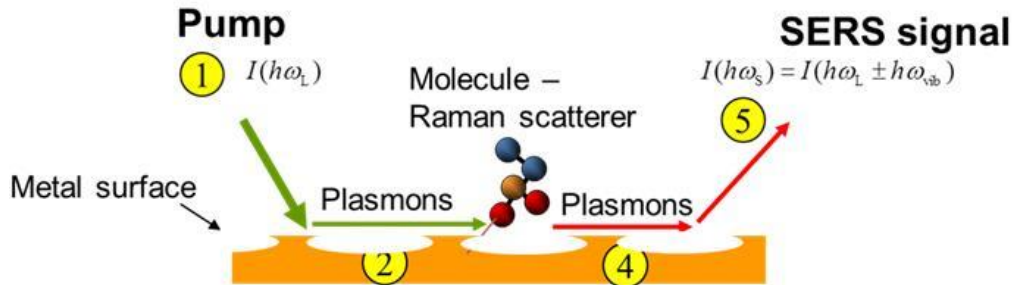
Replacing (2) in (1) we have:

$$\begin{aligned} \Delta G^* &= \frac{4}{3} \pi \left( -2 \frac{\gamma}{\Delta G_v} \right)^3 \Delta G_v + 4 \pi \left( -2 \frac{\gamma}{\Delta G_v} \right)^2 \gamma \\ &= \frac{4}{3} \pi \left( -8 \frac{\gamma^3}{\Delta G_v^3} \right) \Delta G_v + 4 \pi \left( 4 \frac{\gamma^2}{\Delta G_v^2} \right) \gamma = -\frac{32}{3} \pi \frac{\gamma^3}{\Delta G_v^2} + 16 \pi \frac{\gamma^3}{\Delta G_v^2} = \frac{16 \pi \gamma^3}{3 \Delta G_v^2} \\ \Delta G^* &= \frac{16 \pi \gamma^3}{3 \Delta G_v^2} \end{aligned}$$

**[3 Marks]**

**B3a. (i) Sketch schematically the plasmon mediated SERS process and clearly indicate on the diagram or list below it the five steps involved.**

a sketch which is similar or has all the major features of the diagram below. The metal surface indicated can be plane or corrugated. [3 marks for a labelled diagram]



The 5 steps to be indicated or listed in sequence are:  
[1 mark for each step]

1. Impinging laser light excites plasmons,
2. these convey optical energy into the molecule,
3. the molecule undergoes Raman scattering
4. this scattered radiation couples into a plasmon at longer wavelength and,
5. this plasmon decays away into an emitted photon.

**(ii) Plasmon absorption spectra for four nanoscale metallic structures A, B, C and D are shown in the figure below. If an excitation laser at 488 nm is used and the Raman scatter is observed at 600 nm for doing SERS experiments, which one of these is likely to show the highest SERS signal and which the lowest? Also give a reason for each of your two choices**

The highest SERS intensity is likely to be shown by B and the lowest SERS signals are likely to be shown by D. [1 mark]

The reason is that signals in surface-enhanced Raman scattering are a product of enhancement provided by surface plasmons at both the excitation wavelength as well as at the scattered wavelength. [1 mark]

Strong plasmon absorption, hence possibility of enhancement, at both the excitation and scattered wavelengths occurs in B and it should therefore show highest signals. [1 mark]

D has strong plasmon absorption at ~550 nm which is neither resonant with the excitation or the scattered wavelength or in other words it doesn't show a strong plasmon absorption at either the excitation or the scattered wavelength (unlike A and C, respectively) and therefore should show the lowest SERS signals. [1 mark]

**B3b. (i) In the following equation of motion for electrons used in the Drude model, m is the electronic mass, r is their displacement, e is electronic charge and E is the electric field; what is  $\Gamma$ ? Will its value be higher or lower for a highly conducting metal compared to a non-conducting metal?**

$$m \frac{\partial^2 r}{\partial t^2} + m\Gamma \frac{\partial r}{\partial t} = -eE$$



$\Gamma$  is the damping constant. Accept friction or retardation, or description such as: it is a constant which signifies the influence of the nuclei on the electrons on damping their motion. [1 mark]. No, its value will be higher in non-conducting metals which have less conduction electrons because that means the electrons are more tightly bound and not free to move, that is, their motion is highly damped. [1 mark]

(ii) Using the above equation and the expressions for periodic  $E$  and  $r$  ( $E = E_0 e^{-i\omega t}$  and  $r = r e^{-i\omega t}$ ) derive an expression for  $r$  in terms of  $m, E, e$  and  $\Gamma$ .

The expression, derived simply by substituting the periodic functions in the equation of motion is

$$r = \frac{eE}{m\omega[\omega + i\Gamma]}$$

[2 marks]

(iii) Using the above derived expression for  $r$ , and given that polarization ( $P$ ) in a material can be written both in terms of displacement ( $r$ ) of electrons as well as material susceptibility ( $\chi$ ) that is,  $P = -Ner = \epsilon_0 \chi E$ , where  $N$  is number of electrons, derive the expression for the dielectric function ( $\epsilon_\omega = 1 + \chi$ ) of the material. Use this expression to define the bulk plasmon frequency ( $\omega_p$ ) in terms of  $N, e, m$  and  $\epsilon_0$ .

Using the expression  $r = \frac{eE}{m\omega[\omega + i\Gamma]}$  derived above and substituting this in the expression

[1 mark]

provided for polarisation  $-Ner = \epsilon_0 \chi E$  gives

$$\chi = \frac{-Ne^2}{\epsilon_0 m\omega[\omega + i\Gamma]} \quad [1 \text{ mark}]$$

Therefore, the dielectric function:  $\epsilon_\omega = 1 + \chi = 1 - \frac{Ne^2}{\epsilon_0 m\omega[\omega + i\Gamma]}$

From where by collecting all the constants in the fraction and noting that  $\omega$  is 2<sup>nd</sup> order one could define  $\omega_p^2$  as  $\frac{Ne^2}{\epsilon_0 m}$

$$\text{Or } \omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m}}$$

**[2 marks]**