SEMESTER 2 EXAMINATIONS 2013-2014

NANOSCIENCE: TECHNOLOGY AND ADVANCED MATERIALS

DURATION 120 MINS (2 Hours)

This paper contains 8 questions

Answer **ALL** questions in **Section A** and **only TWO** questions in **Section B.**

Section A carries 1/3 of the total marks for the exam paper and you should aim to spend about 40 minutes on it.

Section B carries 2/3 of the total marks for the exam paper and you should aim to spend about 80 minutes on it.

An outline marking scheme is shown in brackets to the right of each question.

A Sheet of Physical Constants is provided with this examination paper.

Only University approved calculators may be used.

A foreign language translation dictionary (paper version) is permitted provided it contains no notes, additions or annotations.

Section A

A1. In diffraction analysis of the atomic structure of materials, the wavelength of the radiation used should be comparable with the atomic separation. Assuming that the latter is on the order of 0.1 nm, calculate the required energy in electron volts for the electrons (using the non-relativistic formula) and photons.

[4 marks]

A2. State the typical kinetic energy of electrons used for transmission electron microscopy with atomic resolution and calculate the corresponding wavelength.
Comment on the difference in electron kinetic energy in A1 and A2.

[4 marks]

A3. (i) What is the fundamental advantage of Surface Enhanced Raman Spectroscopy (SERS) over Raman spectroscopy? What might be a disadvantage?

(ii) What is the momentum matching condition for obtaining a surface plasmon resonance in the Kretschmann configuration (total internal reflection methods)? If the refractive index of the prism is changed from 1.2 to 1.5, what will change and why? Explain very briefly taking into account the answer to the first part of the question.

[4 marks]

A4. What are the effects on the reactivity, melting temperature, phase stability and phase transition when going from a solid bulk material to a nanoscale material? Explain your answers.

[4 marks]

A5. What is the bottom-up synthetic approach? What drives this approach? Name three synthetic methods where the bottom-up approach is employed. [4 marks]

SECTION B

B1.

(a) (i) Why do 10 nm silver nanoparticles not fluoresce as 5 nm colloidal CdSe dots do? Draw a graph of the density of states in each case.

[7 marks]

(ii) Explain how the emission spectrum of a CdSe nanoparticle changes when its size grows from 2.5 nm to 4.5 nm.

[3 marks]

(b) Discuss the differences in the absorption spectra (in terms of number of peaks, intensity of the plasmon band and wavelength of the maximum absorption) of:

(i) a silver sphere of 40 nm diameter and a silver tetrahedron of the same dimensions.

(ii) a silver sphere of 40 nm diameter, and a silver cube with sides of length 40 nm.

(iii) a silver octahedron of side length 40 nm and a silver cube of side 40 nm.

[6 marks]

(c) Write down an approximate expression for the quantum mechanical tunnelling probability of a particle across a finite one-dimensional rectangular potential barrier of width d and height W. Assuming that the workfunction of an STM metal tip is 5 eV estimate the change in tunnelling current caused by increasing the gap spacing by 0.1 Å.

[4 marks]

TURN OVER

B2.

(a) (i) The ratio between anti-Stokes (aS) and Stokes (S) peaks in normal Raman scattering is related by the expression:

$$\frac{I_{aS}}{I_S} = \left(\frac{\nu_{aS}^4}{\nu_S^4}\right)\exp(-h\nu_R / k_b T)$$

where ν_S and $\nu_{\alpha S}$ are the scattered frequencies at the Stokes and anti-Stokes wavelengths, ν_R is the Raman shift (vibration) frequency, h is the Planck's constant, k_b is the Boltzmann's constant and T is the temperature. Hence, in principle one could calculate the temperature of the material from a full (Stokes and anti-Stokes) Raman spectrum or calculate the expected $\frac{I_{aS}}{I_S}$ ratio for a given line at a particular temperature.

Ignoring the $(\frac{\nu_{aS}^4}{\nu_S^4})$ frequency dependence, find the expected $\frac{I_{aS}}{I_S}$ ratio at room temperature (25^{o}C) for the Raman peak of silicon at 520 cm^{-1} (shown in the spectra given in the figure 1), and compare it with the actual value read from the spectrum. Suggest a reason for any discrepancy you observe. If appropriate, use approximations and conversion factors (k_bT ~0.025 eV at room temperature; 1000 cm^{-1} hc ~ 0.125 eV). Calculate and explain how the anti-Stokes/Stokes ratio of peak intensities ($\frac{I_{aS}}{I_S}$) would change if a Raman measurement is taken with the silicon heated to 800^{o}C.

[8 marks]

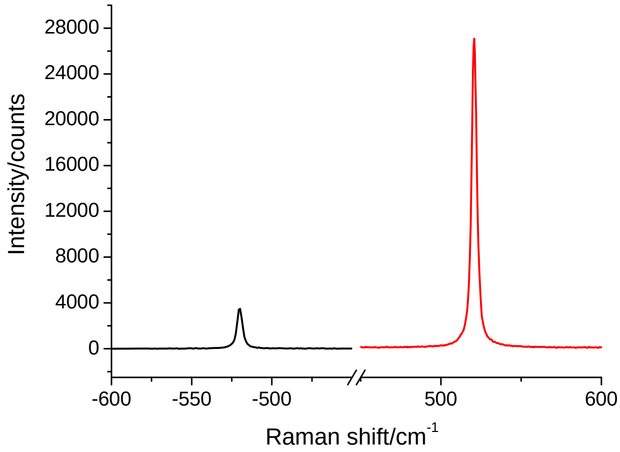

Figure 1. Stokes and anti-Stokes Raman spectra of silicon taken with a 633 nm laser

(ii) How is electric field enhancement related to the intensity of signals in surface-enhanced Raman spectroscopy (SERS)? If a nanoscale structure enhances the electric field at the excitation wavelength by 20 times and the scattered field by 25 times, what will be the enhancement factor (EF) observed in SERS compared to conventional Raman spectroscopy?

[4 marks]

(b) (i) What is self-assembly? What are the principles of molecular self-assembly?

[3 marks]

(ii) Name five ways that the self-assembly of block copolymers can be directed.

[3 marks]

(iii) Name two self-assembly interactions that take place between two DNA strands.

[1 mark]

(iv) What is ionic self-assembly?

[1 mark]

TURN OVER

B3.

(a) (i) Draw a sketch of solute concentration versus time during the nucleation and growth of a nanoparticle. Discuss the nucleation and growth process.

[6 marks]

(ii) Assume that gold nanoparticles have a spherical shape and a uniform fcc crystalline structure. Show that the average number of atoms per nanoparticle can be calculated using the following formula:

$$N = \frac{D^3 \pi \rho N_A}{6 M_w}$$

where N is the number of atoms per nanoparticle, ρ is the density of the gold atoms in the fcc lattice, D is the average diameter of nanoparticles, M_w is the molecular weight and N_A is the number of gold atoms per mole

[4 marks]

(b) Consider a two-dimensional square metallic island with sides of length a = 0.18 nm on top of a metal surface. The tip of a scanning tunnelling microscope (STM) is placed above the centre of the island and a $\frac{dI}{dV}$ spectrum is measured, where I is the tunnelling current and V is the bias voltage.

(i) Explain qualitatively under what conditions peaks can be observed in the $\frac{dI}{dV}$ versus V spectrum.

[1 mark]

(ii) Determine the bias voltages at which the first 2 peaks in the $\frac{dI}{dV}$ versus V spectrum appear, assuming that the island can be modelled by an infinite square well. The effective mass of electrons in the island is m_e^* = 0.46 m_e and the bottom of the surface state band is 0.40 eV below the Fermi level.

[7 marks]

(iii) Sketch the spectrum that would be obtained and indicate the relative strengths of the peaks to be expected

[2 marks]

END OF PAPER