Characterization of nanoparticles through medium-energy ion scattering (MEIS)

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Abstract

In this work we review the use of the MEIS technique to characterize nanostructures at the surface of a substrate. We discuss here how the determination of shape and size distribution of the nanoparticles is influenced by the energy-loss at the backscattering collision, which leads to an asymmetrical energy-loss line shape. We show that the use of a Gaussian line shape may lead to important misinterpretations of a MEIS spectrum for nanoparticles smaller than 5 nm. The results are compared to measurements of gold nanoparticles adsorbed on a multilayered film of weak polyelectrolyte.

Introduction

Nanotechnology has brought some new challenges, not only for the development of new processes for synthesis of nanostructures but also for the characterization of them. The latter is usually achieved by techniques involving incident electrons or photons (e.g. electron microscopy, X-ray spectroscopy and diffraction, and ultraviolet–visible spectroscopy), and to a less extend by using incident ions (e.g. Rutherford backscattering spectrometry – RBS) [1].

Determining the depth distribution of different chemical elements near and at the surface of solids is of major importance for many aspects of nanotechnology. In principle, this can be accomplished quantitatively with deep subnanometric depth resolution, using ion scattering at energies corresponding to the maximum stopping power and high-energy resolution detection systems. The method is called medium energy ion scattering (MEIS) [1,2] and uses typically 100-200 keV incident H^+ or He^+ ions, and combines effects of elastic recoil energy loss and inelastic losses, as in a conventional Rutherford backscattering. The MEIS technique is widely used for analysis of microelectronic materials as well as for the determination of structural and vibrational parameters of crystalline surfaces [3].

More recently, the MEIS technique was used as an additional tool for characterization of Pt-Rh [4] and Au nanoparticles [5] and of InAs-GaAs quantum dots [6] Basically the nanoparticles shape, composition, size distribution and stoichiometry have been successfully obtained. In addition, the determination of the number of nano-size inhomogeneities in thin films was also investigated for some particular geometrical shapes. Nevertheless, the most promising MEIS application, namely the determination of depth distributions of different elements in a single nanoparticle, still needs further investigations. This possible MEIS application is unique and is hardly achieved by any other analytical technique.

In this work we developed a Monte Carlo simulation of MEIS spectra that considers any nanoparticle geometry and areal density, going beyond previous investigations that were restricted to few specific nanostructures shapes and surface coverage [7]. The present method also includes the effect of the asymmetry of the energy-loss distribution due to a single violent collision such as the backscattering event. Using this method we investigated the influence of the nanoparticle geometry, areal density, size distribution, and energy-loss line shape on the 1D (energy) and 2D (energy and angle) MEIS spectrum.

MEIS technique

MEIS is based on the same principles of Rutherford backscattering spectrometry (RBS), however the implementation and data analysis of MEIS is somehow different. A toroidal electrostatic energy analyzer, with a much larger solid angle, replaces the surface barrier detector used in RBS analysis. The system presents a much better energy resolution, typically dE/E of about 10^{-3}, meanwhile both the energy and the scattering angle are simultaneously stored in a 2D multichannel system.

The experimental work was performed at the Ion Implantation Laboratory of the Physics Institute (Federal University of Rio Grande do Sul). A 500 kV electrostatic accelerator provided beams of H^+ at a nominal energy of 100 keV. The samples were mounted in a 3-axis goniometer inside the analysis chamber kept under a pressure of about 10^{-7} mbar. Typical ion current was less than 15 nA and the samples was moved each 4.5 C in order to avoid damage of the nanoparticles. Details of the data analysis are found in ref[8]

Simulation procedure

General formulas to simulate MEIS or RBS spectra were proposed only for particular shapes of nanostructures such as for spherical and columnar nanoparticles (or inhomogeneities) [9]. Here we followed a quite general approach, where any nanoparticle geometry, inclusions, porous, inhomogeneities, and their corresponding areal and size distributions are accounted for. To this end, we use the Monte Carlo method for the 3D-spacial integrations and determine the incoming- and outgoing-projectile paths numerically from the incident and scattering angles. The best way to determine the shape of a nanoparticle through the MEIS technique is to look at all different scattering angles available since each geometrical shape has a typical angular dependence of the backscattering yield. For normal incidence, figure 1 shows this angular dependence for the 4 geometries and beam parameters mentioned above. The overall features are the following. As well known, for films, the decrease of the highest backscattering energy (the front edge in a 1D MEIS spectrum) with increasing scattering angle is only due to the variation of the kinematical factor K. The rapid decrease of the lowest detected energy for smaller scattering angles is a direct consequence of the enhanced path length (by the factor 1/cos(Θ)) in a grazing detection direction. Thus, the energy-loss spectrum is much wider at smaller scattering angles. In the case of a spherical nanoparticle, as depicted in Fig. 1, we have the opposite. In normal incidence, the maximum path length of two diameters is found at the scattering angle of 180 degrees, which makes the energy-loss wider at large scattering angles. For the hemisphere (see Fig. 1), the enhancement of the path length at larger scattering is not as important as in a sphere, neither the enhancement at smaller scattering angle is as large as in a film. In this way, the lowest energy edge will depend weakly on the scattering angle. Finally, the cylindrical geometry (representing disks, wires or columnar structures) is peculiar because the energy spectrum is widest at an intermediate scattering angle, where the outgoing particles can travel along a major diagonal of the cylinder. Thus, MEIS could easily identify uniformly right or oblique cylinders.

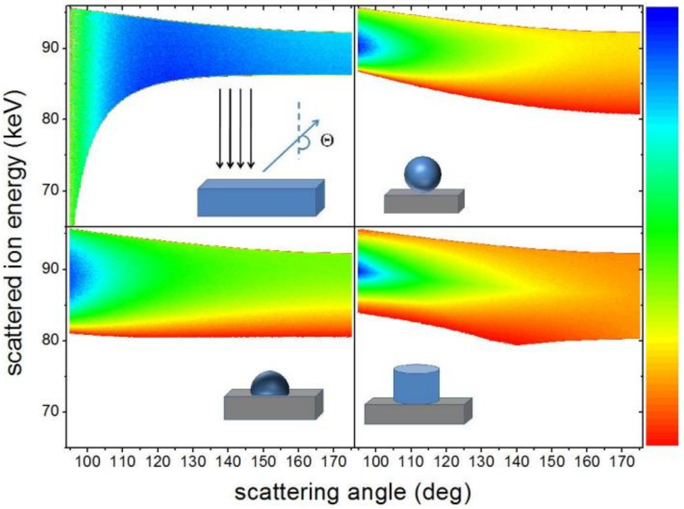

Fig.1:Two-dimensional map of scattered ion intensities as a function of scattering angle and scattered ion energy for incidence of 100 keV He+ ions.

Comparison with experimental data

A sample containing Au nanoparticles were prepared using the layer-by-layer (L-b-L) process to get nanoparticles with specific size through methodology [10]. Here, the polyelectrolyte multilayer (PEM) was used to bind nanoparticles. This process involves deposition of weak polyelectrolytes from diluted aqueous solution, based in electrostatic interactions of opposite polymer charges, on specific substrates. . The samples were first characterized by transmission electronic microscopy (TEM) using JEOL 200CX operated at 120 kV. The Au nanoparticles image and the inset for the corresponding size distribution are found in Figure 2. The gold nanoparticles obtained are spheres with mean diameter of about 11.2 nm. The experimental and simulated MEIS energy-angle spectra for the gold nanoparticle described above are shown in Figure 3. The simulation was performed considering spherical Au nanoparticles separated from each other by 8 nm and the best fit criterion was the minimum chi squared for 3 different scattering angles. The agreement is very good and the remaining differences can be attributed to a better description of the target. In fact, overlapping nanoparticles and their distribution in depth and distance from each other were not included in the simulation. Overlapping nanoparticles are visible in the TEM cross-view image, but they are the result of projection on the transversal plane. If we have considered any other geometry, the resulting 2D spectra would be significantly different from the experimental one. Concerning the determination of size distribution of nanoparticles, the uncertainties are about 5 % for the mean diameter and 15% for the Two-dimensional map of scattered ion intensities as a

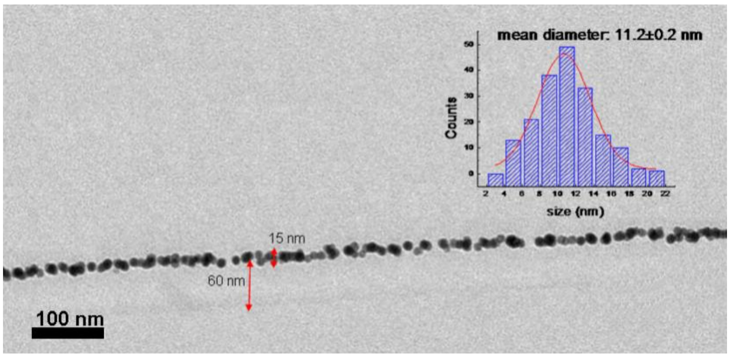

Fig.2:TEM image and size distribution of gold nanoparticles (inset).

function of scattering angle and scattered ion energy for incidence of 100 keV H ions. The experimental data are shown on the left and theoretical simulation on the right.

For the present case of nanoparticles with mean diameter of about 11nm, the use of the Gaussian energy-loss distribution would affect the prediction of the mean diameter by only 3%. The comparison of the full energy-angle distributions is a unique feature of the present simulation Two-dimensional map of scattered ion intensities as a function of scattering angle and scattered ion energy for incidence of 100 keV H ions. The experimental data are shown on the left and theoretical simulation on the right. Two-dimensional map of scattered ion intensities as a function of scattering angle and scattered ion energy for incidence of 100 keV H ions. The experimental data are shown on the left and theoretical simulation on the right.

Conclusions

The main results of the present investigation can be summarized as follows: a) we observed that, although the influence of the energy-loss distribution on the MEIS spectrum is significant only for small nanoparticles (diameter < 5 nm), the use of the actual nanoparticle geometry is important for all sizes of nanostructures;b) neglecting the asymmetry of the energy-loss leads to a false nanoparticle size distribution in the case of small nanoparticles; c) the method used here is the first to our knowledge not restricted to a few nanoparticles shapes and surface coverage.

Finally, we used the method described here to simulate MEIS spectra and determine the shape and size distribution of gold nanoparticles adsorbed on a multi-layered film of weak polyelectrolyte. The parameters obtained for the nanoparticles from the simulation of experimental MEIS spectra agrees quite well with an image obtained by transmission electron microscopy (TEM) of the sample.

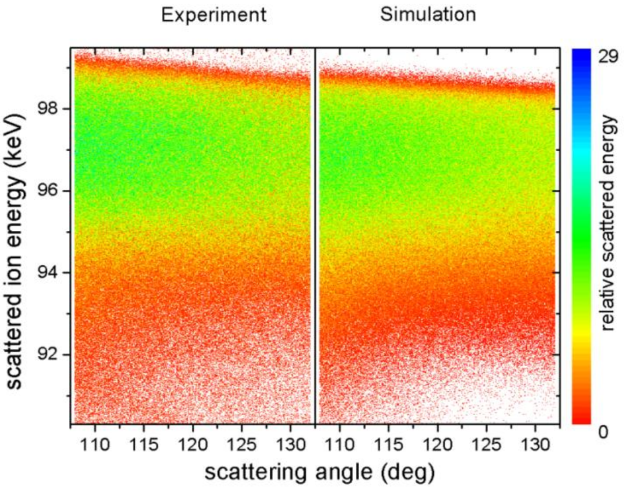

Fig.3 Two-dimensional map of scattered ion intensities as a function of scattering angle and scattered ion energy for incidence of 100 keV H ions. The experimental data are shown on the left and theoretical simulation on the right.

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