New approach for structural characterization of planar sets of nanoparticles embedded into a solid matrix

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In this work we demonstrate that Medium Energy Ion Scattering (MEIS) measurements in combination with Transmission Electron Microscopy (TEM) or Grazing Incidence Small Angle X-Ray Scattering (GISAXS) can provide a complete characterization of nanoparticle (NP) systems embedded into dielectric films. This includes the determination of the nanoparticle characteristics (location, size distribution and number concentration) as well as the depth distribution and concentration of the NP atomic components dispersed in the matrix. Our studies are performed considering a model case system consisting of planar arrangements of Au NPs (size range from 1 to 10 nm) containing three distinct Au concentrations embedded in a SiO2 film.

The physical properties of metallic nanoparticle (NP) systems embedded in dielectric substrates depend not only on the NP parameters (location, size distribution and number concentration) but also on the quality of the dielectric matrix around the NPs. This applies for photonic devices1 and most particularly for the development of nonvolatile, high areal number density and low power memory devices2–4. Degraded dielectrics allow trap-to-trap tunneling processes reducing the charge accumulated in the NPs, while high quality dielectrics improve the memory window, its write/erase speed and its retention and endurance properties5,6. The impurity content of a dielectric matrix is a critical degradation issue. The NPs system itself can be regarded as one major source of matrix impurities. The NPs are thermodynamically unstable and lead to the formation of a solute concentration field of their constituent atoms dissolved within the surrounding matrix as provided, for example, by the Gibbs–Thomson effect7. For Ge NPs in silica, empirical evidence shows that a significantly high fraction of the total Ge content in the sample (from 20 to 70%) may remain dissolved in the matrix even after high temperature thermal treatments8–10. In this case it is argued that, since Ge and Si behave similarly with respect to the formation of tetrahedral bonding structures, Ge atoms could indeed replace Si ones in the SiO2 lattice and therefore present a high solubility limit. In contrast, for other elements with distinct chemical properties, it is generally expected a rather low solubility limit. However, for NP systems produced under non thermodynamic-equilibrium conditions, solute concentrations are difficult to predict and may achieve sufficiently high values treading the quality of the surrounding dielectric matrix. Hence, it seems worthwhile to develop reliable techniques and methodologies to investigate and characterize NP systems embedded in a solid matrix, not only determining their microstructure properties (size distribution, shape and space arrangement) but also the characteristics of the corresponding solute field.

In the present contribution we demonstrate that Medium Energy Ion Scattering (MEIS) measurements and Rutherford Backscattering Spectrometry (RBS), in combination with pertinent data from Transmission Electron Microscopy (TEM) and/or Grazing Incidence Small Angle X-ray Scattering (GISAXS) can indeed provide a rather complete and accurate characterization of buried NP systems. Our studies are performed considering a model case system consisting of planar arrangements of Au NPs containing three distinct Au concentrations embedded in a SiO2 film.

GISAXS and TEM are well-established techniques to investigate microstructural properties of such NP systems11,12. Only recently, the potential of MEIS as a tool for the characterization of shape, sizes, local composition...
and stoichiometry of NPs systems has been more systematically explored, but mostly for surface located nanostructures\(13-16\). For more complex systems the MEIS potentialities can be significantly enhanced with the aid of simulation codes such as the PowerMEIS\(17,18\). This code also accounts for multiple scattering effects, which otherwise tend to blur the information extracted from buried NP systems\(19\). In the present contribution we demonstrate that, it is possible to obtain detailed information not only on the microstructure properties of the Au NPs but also on the dissolved part of the Au content (atomically or as small clusters with a few tens of atoms), which was quantified according to their concentration and the depth distribution.

**Results**

Figure 1 shows cross-section sketch to illustrate the samples layout. Figures 1b–e presents cross-sectional and plan-view TEM micrographs obtained from samples deposited during 25 and 100 s. Planar sets of Au NPs, apparently of the Volmer–Weber type\(19\), are observed for all cases including the 50 s deposited sample (not shown). The plan view micrographs directly allows the determination of the NPs areal densities corresponding to: \((13 \pm 1) \times 10^{10} \text{ NPs cm}^{-2}\) for the 25 s deposition case, \((11 \pm 1) \times 10^{10} \text{ NPs cm}^{-2}\) for the 50 s case and \((15.3 \pm 0.5) \times 10^{11} \text{ NPs cm}^{-2}\) for the 100 s case. The total amount of the deposited Au measured by MEIS (and confirmed by RBS measurements) for the 25, 50 and 100 s samples are 1.8, 3.1 and \(7.4 \times 10^{15} \text{ Au atoms/cm}^2\), respectively. Taking into account the total amount of deposited Au, MEIS simulations were carried out using the PowerMEIS code\(22\). An analysis without considering the TEM data could lead to unrealistic results since there are many free parameters in the simulation. Therefore the NP sizes and number concentration obtained by TEM were used as an input to the simulations\(20\). In order to simulate a MEIS spectrum one has to assume a particular geometrical shape, atomic composition and density. In the present case we assumed 2D arrays of spherical NPs with given radius and areal density. Since the total amount of atoms is fixed, only the NP radius was adjusted.

The simulated spectra are then compared with the measured ones as illustrated in Figure 3. This figure shows the ion scattering intensity maps as a function of ions scattering angle and energy for the three measured samples. The columns representing the measured and calculated spectra are labeled “experimental” and “simulation”. Best fits are determined by the minimum of the reliability function \(R^2\) that reads

\[
R^2 = \frac{1}{N} \sum_{i=1}^{N} \left( I_{\text{Sim}} - I_{\text{Exp}} \right)^2.
\]

Here, \(I_{\text{Sim}}\) and \(I_{\text{Exp}}\) correspond to the simulated and measured ion scattering intensities for scattered angles ranging from 108° to 132° and for scattered energies ranging from 105 to 127 keV. The angle and energy ranges were chosen in order to cover exclusively the Au signal. The calculated spectra in Figure 3 correspond to the best fit obtained by the \(R^2\) criteria.

Figures 4a to 4c show how the reliability function \(R^2\) varies with the NPs radius. The full circles correspond to simulations and the lines are parabolic fittings. The best fit is given by the minimum of the reliability function. The corresponding radius and their uncertainties are indicated in each plot.

Figure 4d shows a comparison of radius determined by the parabolic fit obtained from the MEIS analysis assuming that all Au atoms are contained in the NPs and the NPs size distributions provided by TEM and GIXAXS. For the 25 and 50 s cases, the TEM and GIXAXS results are consistent with each other and significantly disagree with the results from the MEIS analysis. Unlike GIXAXS and TEM, the MEIS probe is sensitive to all Au atoms, regardless if they are contained in NPs or dispersed in the matrix. Hence, for a number density of NPs consistent with the one determined from the plan-view TEM micrographs (see Figure 1), this disagreement indicates that part of the deposited Au content is indeed not contained in TEM or GIXAXS detectable NPs, but rather dissolved in the matrix.

In addition, by taking into account the NPs’ size distributions of the samples from GIXAXS analysis (Figure 2d and 2e), the total amount of Au detected by MEIS and RBS and the NPs number densities from plan-view TEM observations, we can state that only...
a small amount of the Au atoms (28 ± 5% for the 25 s sample and 39 ± 9% for the 50 s sample) is actually contained in the NPs. These results are summarized on Table 1. The table also includes the results obtained for the 100 s deposited sample, evaluated considering the size distribution from TEM measurements. For this case we notice that the NPs’ mean size obtained by MEIS analysis is slightly larger than the one by TEM, with overlapping uncertainty bars.

The large differences between GISAXS and TEM as compared to the MEIS results can be attributed to the fact that the samples were prepared in conditions away from the thermodynamic equilibrium and therefore a significant fraction of Au atoms have not been incorporated into the particles during the deposition process. Furthermore, during the deposition of the SiO2 cap layer, it is also possible that additional Au atoms may be re-dispersed from the particles into the silica over layer.

Discussion

Hence, in order to refine the system characterization, additional MEIS simulations were then performed accounting for the dissolved Au content for the 25 and 50 s sample cases. The basic idea of the simulation concept is illustrated in Figure 5a. It introduces a matrix layer with thickness h and composition (SiO2)xAu1–x between the thermally grown and the deposited SiO2. Figure 6b to 6g shows the corresponding MEIS simulations compared to the experimental scattered intensity profiles for three different scattered angles (109°, 120° and 131°). Two different simulations were performed: 1) with (dashed blue line) and 2) without (continuous red line) the...
inclusion of the dissolved part of Au. This comparison highlights the lack of Au when only the NPs are taking into account.

Since the surrounding layer contains the missing gold detected by MEIS and RBS, the thinner layers have larger Au concentrations, as indicated in the x-axis in Figure 7, from where the best fitting was obtained by minimizing the reliability factor $R^2$ in the same way as done before. The results are shown in Table 2. This procedures show that the combination of TEM and/or GISAXS results with MEIS measurements may provide a consistent description of the system microstructure accounting for the NPs and the dispersed atoms in the matrix. It also tackles a refined way to investigate atomic processes of nanoparticle growth under non-thermodynamic equilibrium conditions.

In this work we investigated three planar sets of buried Au NPs embedded into SiO$_2$ matrix synthesized with different sputtering deposition times. We observed that, for the samples prepared with 25 and 50 s, a significant fraction of the total amount of Au atoms becomes dissolved within the dielectric matrix around the NPs. Combining MEIS, RBS, TEM and GISAXS measurements, we were able to quantify the fraction of Au atoms effectively contained in the NPs, as well as the concentration and depth distribution of the complementary Au amount dispersed in the matrix around the NPs. These results open new perspectives for a more complete characterization of embedded metallic NPs systems into a solid matrix and the improvement NP bases devices.

**Methods**

Au atoms were deposited onto 200 nm thick SiO$_2$ films, thermally grown from (001) Si wafers. The deposition was performed by RF magnetron sputtering, in a pure Ar plasma and with an RF power of 20 W, using an AJA magnetron sputtering device (ATC Orion-8 UHV from NANOLAB, Institute of Physics - UFRGS). A set of three samples containing different amounts of Au were obtained considering deposition times of 25, 50 and 100 s. Without breaking the vacuum, immediately after the Au deposition the samples were covered with a 35 nm thick layer of SiO$_2$, deposited using similar conditions but with an RF power of 90 W for 67 min.

| Sample | NPs areal number density (NPs/cm$^2$) | Size distribution | Au present as NPs (%) |
|--------|--------------------------------------|-------------------|----------------------|
| 25 s   | $(13 \pm 1) \times 10^{11}$          | GISAXS            | $28 \pm 5$          |
| 50 s   | $(11 \pm 1) \times 10^{11}$          | TEM               | $59 \pm 5$          |
| 100 s  | $(15.3 \pm 0.5) \times 10^{11}$      | GISAXS            | $39 \pm 9$          |
|        |                                      | TEM               | $53 \pm 9$          |
|        |                                      | TEM               | $112 \pm 7$         |
These samples were then directly investigated by MEIS, RBS, TEM and GISAXS. The MEIS measurements were performed using a 150 keV He$^+$ ion beam. The samples were mounted in a 3-axis goniometer inside the analysis chamber kept under a pressure of about 10$^{-7}$ mbar. Typical beam current was less than 15 nA. The angle of incidence used was of 10° and backscattered He$^+$ ions emerging from the target were analyzed using a Toroidal Electrostatic Analyzer (TEA) mounted at 120 degrees with respect to the beam direction. At the top end of the TEA a set of two micro-channel plates coupled to a position-sensitive detector allows each ion to be energy- and angle-analyzed leading to 2-D spectra. The TEA angular aperture is 24 degrees and each angle bin corresponds to 0.08 degrees. The overall energy resolution of the system is 600 eV. Details of the data analysis are described in refs. 17–19, 22. The MEIS analysis was performed using the 500 kV electrostatic accelerator from the Ion Implantation Laboratory (LII), IF–UFRGS. The MEIS measurements were analyzed using the PowerMEIS package$^{22}$ where the sample is discretized layer by layer using full 3D matrices. Each one represents a layer, and each element of the matrix stands for specific composition, stoichiometry and density of the material. In this way the set of NPs was generated with specific shapes, size and pair correlation function. The PowerMEIS program can handle any geometric shape, size distribution, and density of the nanostructures. It also accounts for the asymmetry of the energy loss-distribution due to the backscattering collision and to multiple scattering effects.

Standard Rutherford backscattering Spectrometry (RBS) experiments were also performed using a 1.4 MeV He$^+$ ion beam from the 3 MV tandem accelerator from the LII-IF-UFRGS. Additional high-resolution observations were carried out in a Cs-corrected FEI Titan 80/300 microscope from the Brazilian National Institute of Metrology (INMETRO). Z-contrast images were acquired through scanning transmission electron microscopy (STEM) using a high-angle annular dark-field detector.

Figure 6 | (a) Illustration of the system characteristics considering the planar set of NPs embedded in a matrix containing Au atoms (i.e. (SiO$_2$)$_x$Au$_y$) distributed in a layer with thickness $h$. (b–g) Results for the 25 and 50 s cases showing the experimental scattered intensities profiles (gray line-circles) as a function of energy for three scattered angles and the simulated ones. The simulations considering the Au content present only in the NPs are shown in continuous red lines. Those considering the NPs and the dissolved Au atoms within the surrounding matrix are represented by dashed blue lines.

Figure 7 | The reliability R2 values (black dots) as a function of the Au concentration in the surrounding layer (SiO$_2$)$_x$Au$_y$, as illustrated in Figure 5. The red lines are eye-guiding curves.
Table 2 | The surrounding layer thickness h and the corresponding Au concentration, both obtained from the minimum value of R² from Figure 7

| Sample | Surrounding layer thickness h (nm) | Au concentration (at.%) |
|--------|-----------------------------------|------------------------|
| 25 s   | 4.0 ± 0.3                         | 5.1 ± 0.4              |
| 50 s   | 5.1 ± 0.7                         | 6.0 ± 0.9              |

(HAADF). The GISAXS measurements were performed in the Brazilian Synchrotron Light Source LNLS, with 8.5 keV of X-ray energy. The GISAXS data were analyzed with the FitGISAXS package developed within the IGOR Pro analysis software (WaveMetrics, Inc.).

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Author contributions

G.M. worked on the modification of the PowerMEIS source code by including Multiple Scattering effects, which is important for buried nanostructures in solid matrix. C.M. worked on the sample synthesis and GISAXS experiments. D.L.B. measured and analyzed GISAXS data using IGOR Pro. A.A. worked on the sample synthesis and GISAXS experiments. D.L.B. measured and analyzed GISAXS data using IGOR Pro.

Additional information

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