

Gold-based nucleation in implanted silica studied by x-ray absorption spectroscopy

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Abstract

Ion implantation into silica is used to produce Au subnanometer metal clusters, whose size can be finely tuned from few-atom to about 1 nm by acting on the implantation fluence and post-implantation annealing conditions. The structural analyses rely basically on x-ray absorption spectroscopy that can investigate the metal site independently from long range order considerations. Besides the signal from the intermetallic coordination, a correlation of the dopant with oxygen atoms from the matrix is found, especially upon implantation at low fluence. The possibility of promoting the formation of subnanometer AuAg clusters by sequential ion implantation is also explored, with promising preliminary results. The control of the metal cluster nucleation, composition and first steps of growth have relevant consequences on the interpretation of the optical emission spectra of these molecule-like clusters and on their sensitizing action towards nearby rare-earth ions embedded in the same matrix. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

In the last decades ion implantation-based routes have been widely demonstrated to be suitable to promote the formation of single metal and alloy nanoclusters in glasses and polymers, with promising application in many fields including plasmonics, sensing and photovoltaics [1–6]. The coupling of ion implantation with proper annealing at defined temperature and atmosphere and/or irradiation by laser or ion beams widens the palette of possible morphologies and compositions. Moreover, alloy nanoclusters whose corresponding bulk phase is unstable or metastable at room temperature can be easily obtained [7,8]. Most of papers deal with the formation of clusters whose size ranges from few to about 10 nm, condition in which the clusters electronic energy levels can be safely approximated with the corresponding metallic bulk ones.

In the last years it has been shown that, by reducing the metal implantation fluence and for moderate annealing conditions, the average cluster size could be reduced down to the size critical for the thermodynamic stability, corresponding to few atom aggregates [9,10]. This is very interesting for a number of reasons. First, the electronic energy levels of clusters of few atoms are intermediate between the atomic ones and the bulk bands and their optical properties vary accordingly [11–13]. Moreover, since the fraction of atoms at the cluster surface is close to one, the interaction of the cluster with the matrix is favored, leading to a modification of the cluster electronic energy levels with respect to those of unsupported clusters [13,14]. Second, the full control of the very early steps of cluster nucleation in a matrix is crucial to obtain a good control of the cluster size distribution in the nanometer range. Thermodynamics considerations allow to estimate the Gibbs free energy required for homogeneous metal nucleation. Nevertheless, it is known that for cluster nucleation in a matrix the energy barrier to be overcome for

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Table 1
Ion implantation conditions for the different sample series.

Sample name	First implantation series total dose (impl. energies)	Second implantation series total dose (impl. energies)
Au0.3	7×10^{14} Er ⁺ /cm ² (190, 100, 50 keV)+800 °C annealing	3×10^{14} Au ⁺ /cm ² (180, 100, 50 keV)
Au0.6	7×10^{14} Er ⁺ /cm ² (190, 100, 50 keV)+800 °C annealing	6×10^{14} Au ⁺ /cm ² (180, 100, 50 keV)
Au3	7×10^{14} Er ⁺ /cm ² (190, 100, 50 keV)+800 °C annealing	3×10^{15} Au ⁺ /cm ² (180, 100, 50 keV)
Au7	7×10^{14} Er ⁺ /cm ² (190, 100, 50 keV)+800 °C annealing	7×10^{15} Au ⁺ /cm ² (180, 100, 50 keV)
Au30	30×10^{15} Au ⁺ /cm ² (190 keV)	–
Au30Ag30	30×10^{15} Au ⁺ /cm ² (190 keV)	30×10^{15} Ag ⁺ /cm ² (130 keV)
Au2Ag1	1.6×10^{15} Au ⁺ /cm ² (180, 110, 60 keV)	1×10^{15} Ag ⁺ /cm ² (140, 80, 45 keV)

heterogeneous nucleation is lower than for the corresponding homogeneous nucleation, but it is not easily determined quantitatively. About the possible practical applications of molecule-like clusters and as a final point, it has been shown that sub-nanometer Au clusters embedded into Er-doped silica, when excited in the UV–vis range, can transfer part of the absorbed energy to the Er ions, dramatically increasing the effective cross section for 1.54 μm Er³⁺ emission, with promising application in photonics [9,15]. This energy transfer process has been tentatively related with the photoluminescence band at 890 nm of small Au clusters, whose origin is thought to be the electronic surface states of gold clusters [13].

X-ray absorption spectroscopy (XAS) [16] is an elective tool to investigate the single-metal and alloy cluster formation in implanted silica: the full analysis of the oscillations in the x-ray absorption spectra above the photoelectric absorption edge from a core state of the metal dopant allows to detect the metal–metal nearest neighbor coordination signal, whose presence marks the onset of cluster nucleation. The possible presence of dispersed oxide phases is also detectable, as well as the interatomic correlation of atoms at the cluster surface with atoms of the surrounding matrix [9]. To experimentally investigate the very early steps of metal nucleation, implanted layers (usually less than 100 nm thick) have a very low metal concentration i.e., in implanted silica metal nucleation occurs for metal density in the range of ≈ 1 at%: the XAS experiments are very demanding in terms of needed photon flux, integration time and required experimental setup [17,18].

In this paper we show experimental results, mainly based on the x-ray absorption spectroscopy on low-fluence metal-implanted silica, with the aim to enlighten the information on the cluster size, cluster–matrix correlation that can emerge when the aggregates are formed of few-atoms.

2. Experimental and data analysis

Single or sequential metal ion implantation (Au or Au + Ag) processes were carried out onto pure silica slides (Herasil I by Heraeus). In some cases, a triple implantation energy scheme for each implanted ion species was used, to obtain a homogeneous concentration depth profile in the implanted region. Since these systems were produced to investigate the interaction of metal clusters with rare-earth ions (not reported here) [9,15], a selection of samples was previously implanted with Er ions and annealed at 800 °C for 1 h in N₂ to activate the

1.54 μm Er emission. The total implantation fluence was measured by Rutherford Backscattering Spectrometry. In Table 1 the implantation parameters are detailed. To monitor the possibility of tailoring the cluster size by annealing, the samples were heated for 1 h at defined temperatures up to 800 °C in selected atmospheres (N₂ or H₂ (5%):Ar). In the following, the sample label indicates the metal implantation fluences in 10¹⁵ ions/cm² units: as an example, sample Au0.6 indicates the sample implanted with a total fluence of 0.6×10^{15} Au⁺/cm².

The x-ray absorption spectroscopy experiment was performed at the Au L₃-edge at the GILDA beamline of the European Synchrotron Radiation Facility-ESRF (Grenoble, France), in fluorescence mode using a multielement high purity Ge detector. Samples were cooled at 80 K to reduce atomic thermal vibrations. The x-ray absorption spectra of the samples with the lowest Au atomic concentration (down to 0.5/1000) were recorded at the ID26 beamline at ESRF, with a high resolution fluorescence detection system [18,19].

The analysis of the EXAFS (Extended X-ray Absorption Fine Structure) spectra was performed by the FEFF8-FEFFTIT 2.98 package [20,21]. Data were fitted within the single scattering approximation in the *R*-space, using theoretical signals calculated for Au–O and Au–Au correlations from Au and Au₂O₃ model structures. The use of asymmetric interatomic distance distributions did not improve significantly the fit quality, and so were not used. Using the Au–Au distance obtained by the fit, the number *n* of atoms per cluster was estimated from the size equation: $d_{\text{Au–Au}}(n) = d_{\text{Au–Au}}(\infty) (1 - A/n^B)$, where $d_{\text{Au–Au}}$ is the interatomic distance ($d_{\text{Au–Au}}(\infty) = 2.88 \text{ \AA}$ for Au bulk), $A = 0.128 \pm 0.009$ and $B = 0.37 \pm 0.03$ [9]. It is worth noting that, although this equation derives from theoretical calculations (mainly DFT-based) for Au clusters in vacuum, data available in the literature on supported or embedded Au clusters agree with it [9,22].

3. Results and discussion

In Fig. 1(a) the Au L₃-edge EXAFS spectra of Au7 and Au30 samples are compared with the corresponding spectrum of a Au foil, measured at the same temperature. The EXAFS oscillations for clusters are much smaller than for the corresponding bulk phase, due to the relevant fraction of atoms at the cluster surface and to higher structural disorder of

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