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Plasma-Induced Size Reduction in Gold Nanoclusters Embedded in a Dielectric Matrix

J. Fandiño[1,*], A. Crespo[2], G. Santana[3], L. Rodríguez-Fernández[2], J. C. Alonso[3], M. F. García-Sánchez[3], A. Ortiz[3], O. Vigil[4], A. Lopez-Suarez[2], and A. Oliver[2]

[1] *Universidad Autónoma de la Ciudad de México, Avenida la Corona 320, Col. Loma la Palma, Gustavo A, Madero, 07160, Mexico D.F., México*
[2] *Instituto de Física, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán 04510, México D.F., México*
[3] *Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán 04510, México D.F., México*
[4] *Escuela Superior de Física y Matemáticas, IPN, Edif. 9, U.P.A.L.M., 07738, D.F., México*

Sandwich structures of silicon-nitride/gold/silicon-nitride with approximate thickness of 40 nm were fabricated by means of inductively-coupled remote plasma enhanced chemical vapor deposition and sputtering. In an intermediate step, nanostructure gold was subject to different surface plasma treatments, varying the plasma treatment time as well as the plasma atmosphere. The resulting structures were studied by high resolution transmission electron microscopy and Rutherford backscattering. As a consequence of plasma treatments, the gold nanoparticles mean size decreases, the particle areal distributions become narrower and the particle shapes evolve from island-like to near spherical symmetry. Oxygen plasma-etch of gold nanoparticles was observed.

Keywords: Nanoclusters, PECVD, *z*-Contrast Images.

1. INTRODUCTION

Size reduction of metallic particles up to nanometric scale leads to several changes in their physical and chemical behavior. This fact has been turned into some interesting potential applications for present and future technology. Among the growing list of examples it worth to mention just a few. The high optical nonlinearity with a fast response of metal nanoclusters embedded in a dielectric matrix makes this kind of structures attractive for all-optical integrated circuits.[1] Gold nanoparticles on different substrates display high catalytic activity.[1–4] The intensification of infrared-active vibrational modes of molecules in close proximity with metallic clusters could be used in characterization studies and exploited as a sensing tool.[1,2,5]

One key feature common for these applications is to gain control over the cluster dimensions and shapes. A number of techniques such as alternating sputtering,[6] ultra-high vacuum deposition using bottom-up assembly,[7] ion irradiation[8] and nanolithography,[9] have been tested in order to meet the standards that nanotechnology industry demands. However, high costs and difficulties in order to integrate some of these approaches into the commercial industry process remain as challenges to solve.

Although plasma treatment of solid surfaces have been used for decades in a number of applications including thin film etch,[10] surface cleaning[11] and polymer surface modification,[12] up to now the effect of a surface cold plasma treatment on the properties of metallic clusters of nanometric sizes has not been explored.

In this work we present a new method in order to reduce the clusters size, which consist in cold surface plasma treatments, varying the plasma exposure time as well as the plasma chemistry in gold nanoclusters embedded in a silicon-nitride (SiN) matrix. The results are presented and discussed.

2. EXPERIMENTAL DETAILS

The samples were deposited following four steps: (1) A thin layer (~20 nm) of SiN was grown on NaCl and quartz substrates by Inductive-Coupled Remote Plasma Enhanced Chemical Vapor Deposition (IC-RPECVD). (2) Gold with a nominal thickness of 1 nm was deposited on the SiN layer by sputtering. (3) The resulting Au/SiN/substrate

*Author to whom correspondence should be addressed.

Table I. Experimental parameters used in each step of sandwich structures fabrication.

Parameter	Step 1	Step 2	Step 3	Step 4
Substrate temperature (°C)	200	Ambient	200	200
Pressure (mTorr)	100	75	10	100
RF Power (W)	150	—	180	150
Ar flow rate (sccm)	70	25	—	70
NH_3 flow rate (sccm)	14	—	14	14
SiH_2Cl_2 flow rate (sccm)	1	—	—	1
Current (mA)	—	40	—	—

structures, with gold on top were subject to a plasma treatment. (4) A SiN film, similar to that of the first step was deposited over the previous Au/SiN/substrate structures.

As a result of the four previous steps, sandwich structures of the form SiN/Au/SiN/substrate were fabricated. Details of the experimental parameters used in each of the steps mentioned above are shown in Table I.

The difference between the samples was introduced in step 3. In the first set of experiments, a NH_3 plasma was applied by varying the exposure time between zero and 300 seconds (0, 30, 60 and 300). RF power and pressure were choose through a process of tried and error in order to avoid damages on the substrate, while the temperature was the same used for SiN films deposition. In a second set of experiments, the plasma nature was change by introducing argon, oxygen, ammonia and hydrogen in the chamber, one at a time. The gas flow rate was varied in each case in order to set the chamber final pressure at 10 mTorr. The plasma treatment time was 300 seconds in all cases.

The deposition of silicon-nitride films and the plasma treatment of the gold clusters were carried out by means of an IC-RPECVD system reported elsewhere.[13] Gold was deposited in a reliable fashion by means of DC-sputtering using a Cressington sputter coater 108 auto deposition system with *in-situ* thickness control. Dark field images of high resolution transmission electron microscopy (HRTEM) were recorded with the aid of a JEOL 2010 FEG instrument. *z*-contrast images were processed with the Digital Micrograph 3.7.0 software by Gatan Inc. The amount of gold was measured by Rutherford Backscattering Spectroscopy (RBS) at the IFUNAM's accelerator (NEC 9SDH-2 Pelletron®) using 2 MeV He++ ions. Quartz slides and NaCl crystal, cut into 1 cm × 1 cm pieces, were used as substrates for RBS and HRTEM characterization, respectively.

3. RESULTS AND DISCUSSION

Dark field images of the sandwich structures are shown in Figure 1 as a function of ammonia plasma treatment time. Figure 1(a) (as-grown samples), display gold particles with an island-like structure, typical of the earlier stages of film growth process. When the gold is exposed to a plasma treatment of 30 seconds (1(b)), the islands break

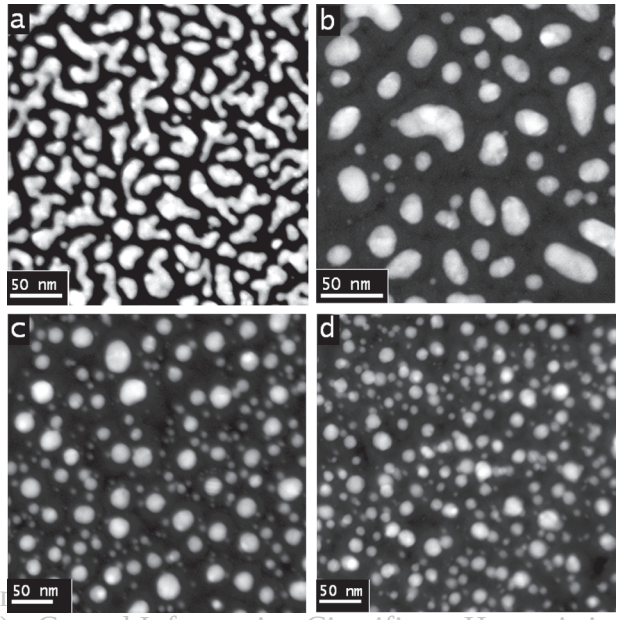

Fig. 1. *z* contrast images of four ammonia plasma-treated samples as a function of the treatment time: (a) 0 s, (b) 30 s, (c) 60 s and (d) 300 s.

and the space between them increases; however they still have enlarged shapes. Further increase of the plasma time exposure (c and d) makes the Au particles smallest with shapes that look near spherical as a first approximation.

The trend in particle sizes shown in Figure 1 must be related with the non-equilibrium nature of the PECVD plasma. In near-equilibrium regimes, an increase in the particle diameters with time is expected due to the Ostwald ripening effect, where matter transfer from small to larger precipitates takes place due to diffusional balance. However, in the non-equilibrium regimes an opposed trend has been observed: larger particles break to form small ones. This behavior is known as inverse Ostwald ripening and has been observed when metallic particles embedded in a dielectric matrix are bombarding with ions (Au, Ar, etc.) at energies over 200 keV.[8, 14, 15] In PECVD systems, the plasma is in the non-equilibrium regime because of the great difference in the electrons and ions temperatures. In this type of discharges, the sheaths are responsible for the acceleration of positively charged ions toward the walls and the substrate. In inductively coupled discharges at pressures using through this work, ion bombarding energies are estimated to lie in the range of 20–40 eV.[16] We believe the ion bombardment of the gold islands expose to the plasma is the main cause of the decreasing in clusters dimensions as the plasma time exposure increases.

The evolution of gold nanoclusters size with plasma treatment is shown in the histograms of the particle diameter distribution (Fig. 2). Besides considering that in general, the shape of the samples do not correspond with spherical geometry, we use the particle diameter in order to our data can be easily compared with those reported in the literature.

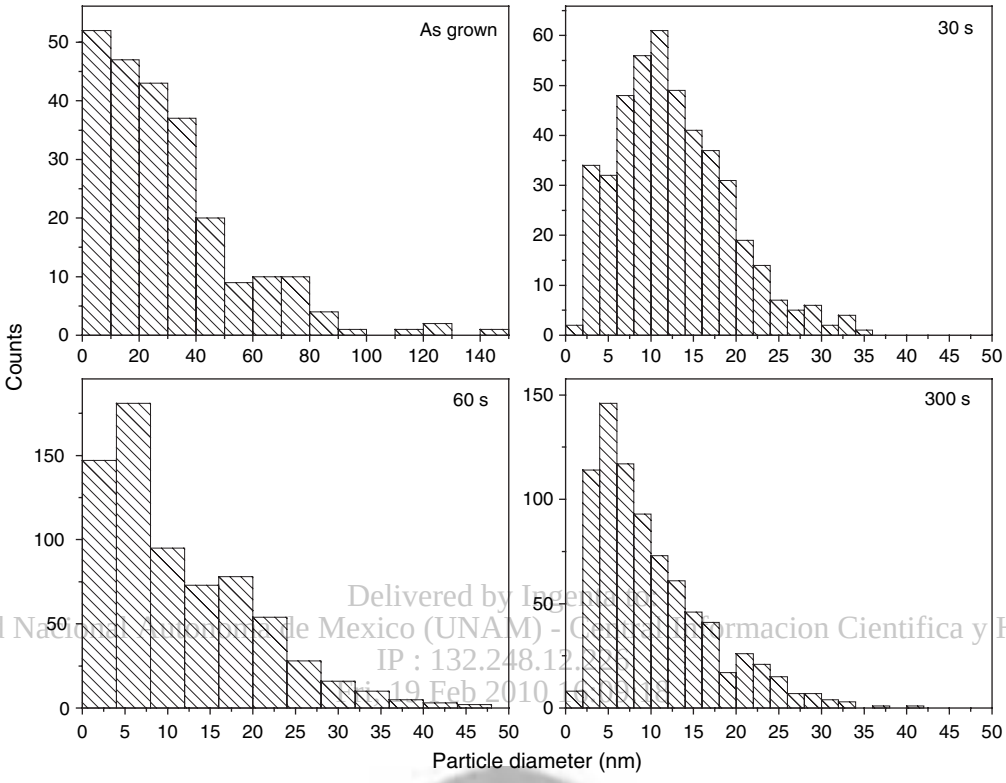

Fig. 2. Histograms of particle mean diameter calculated from images of Figure 1.

The as-grown sample has a non-symmetric, unimodal distribution of particle size, with a great fraction of particles having relatively small diameter. When the plasma treatment time increases, the particle size distributions become narrower and the mean particle diameter displaces to lower values. However, the shape of the distribution does not change much with the plasma treatment time.

Considering the chemical component of the plasma-matter interactions, the observed decrease in particle diameter could be also caused by plasma-etch of the gold clusters. If there is any kind of plasma-etch of gold particles, this would be reflected by decreasing the areal concentration of gold as a function of plasma treatment time. Then, RBS measurements were performed on the samples, taking advantage of the separation in energy between Au and the elements of the SiN matrix and SiO_2 substrate. The results for the areal concentration of Au are shown in Table II.

Table II. RBS data of Au concentration as a function of the ammonia plasma treatment time.

Plasma treatment time (s)	Au concentration (cm^{-2})	Mean diameter (nm)	Standard deviation (nm)
0	2.0×10^{16}	30	24
30	2.0×10^{16}	13	7
60	1.9×10^{16}	11	8
300	2.0×10^{16}	10	7

From the results shown in Table II for Au areal concentration, we conclude that in the ammonia plasma treatment at conditions shown in Table I, there is no evidence of plasma-etch of gold particles. Instead, Au clusters are redistributed across the surface, becoming smallest as the plasma treatment time increases.

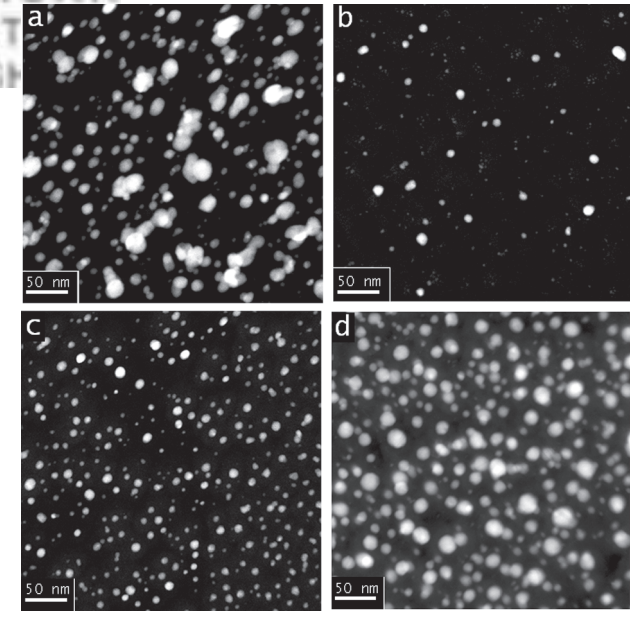

Fig. 3. z contrast images of four plasma-treated samples as a function of the plasma nature: (a) Ar, (b) O, (c) H and (d) NH_3.

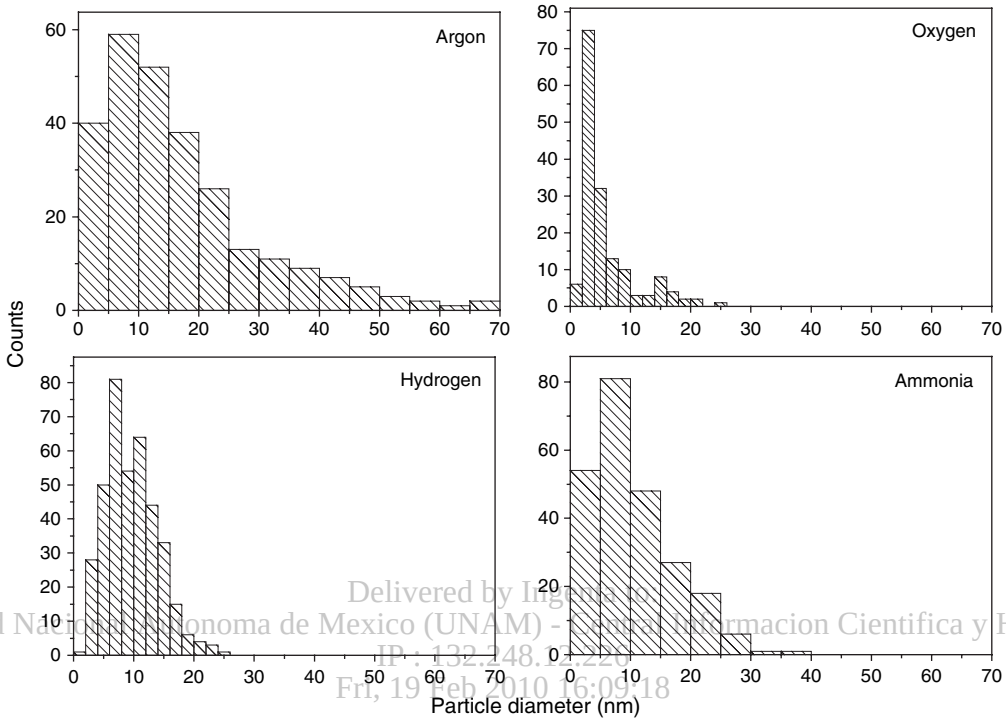

Fig. 4. Histograms of particle mean diameter as a function of the plasma nature.

Anyway, the role of chemical factor in the plasma-gold particles interaction must be analyzed. From this point of view, the nature of the plasma treatment was change and *z*-contrast images for argon, oxygen, hydrogen and ammonia plasma treatments are depicted in Figure 3.

As a general trend, in spite of the atmosphere used, the plasma treatment tends to break the gold islands (Fig. 1(a)) into small clusters of near spherical shape. In Figures 3(a) and (c) can be observed that Ar and H plasma application produces near similar results as the observed in NH_3 plasma (Fig. 3(d)). As the inert nature of the Ar makes very unlikely a chemical reaction of Ar related species with gold particles, we expected these plasma-induced particles evolution obey to a physical interaction as was suggested before for NH_3. However, the relatively small amount of Au particles in Figure 3(b) compared with those shown in images 3(a, c and d) suggest that a possible etch of gold by the oxygen plasma occurred.

The histograms of the diameter distributions as a function of the plasma atmosphere are presented in Figure 4. From these results is clear that for the same treatment time, hydrogen and oxygen have a more pronounced effect in reducing the particle diameter than ammonia and argon (also, the particle diameter distribution are bimodal for H and O and unimodal for Ar and ammonia), indicating that plasma chemistry is an important issue in cluster size modification by plasma and therefore cannot be ignored.

Au areal concentration obtained from RBS measurements of the structures treated with different plasmas are shown in Table III. A reduction of an order of magnitude in Au concentration is reported for the oxygen plasma treatment. This result could be explained in terms of oxygen plasma etching of the gold particles, due to an increase in gold chemical reactivity at nanometric sizes, nevertheless the mechanisms involve in this behavior are unclear at this point.

Table III. RBS data of Au concentration as a function of the plasma nature.

Plasma nature	Au concentration (cm^{-2})	Mean diameter (nm)	Standard deviation (nm)
None	2.0×10^{16}	30	24
Ammonia	2.0×10^{16}	10	7
Argon	1.6×10^{16}	17	13
Hydrogen	1.5×10^{16}	10	4
Oxygen	3.6×10^{15}	6	5

Among the different atmospheres tested in the plasma treated sandwich structures we observed that, for a fixed treatment time, the hydrogen plasma is more efficient than the rest, breaking the larger islands into smaller particles without etch them. Meanwhile, the oxygen plasma produces the smallest particles by a combined effect of break and etch.

4. CONCLUSIONS

We have demonstrated that the application of cold plasmas under certain conditions decreases the size of gold nanoclusters grown on silicon-nitride. The effect can be obtained in two different ways: increasing the plasma time

exposure or change the plasma chemistry. The increase of time makes the Au clusters smaller with near spherical shape. Argon, ammonia and hydrogen plasmas lead to smallest clusters with a narrower mean size distribution, without changing the amount of Au in the sample. The oxygen plasma produces smallest gold cluster but decreases the gold areal concentration by an order of magnitude, due to oxygen plasma etch of gold particles.

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