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Monitoring and modeling the deposition of metal nanoparticles on surfaces by capacitance

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Abstract

The study of metallic nanoparticles (NPs) on surfaces and their properties has become a common subject for a variety of areas. Notably, in order to exploit the unique intrinsic features of deposited NPs, **samples having low coverage are required**. The sample characterization by electrical techniques has, however, so far been limited mostly to systems near or beyond the percolation limit, when the film's resistive behavior is dominant. Here we describe the capacitive response of interdigitated electrodes (IDE) during Ag NP deposition, from the very beginning up to the percolation limit. Our experiments present two regimes: up to 20% of coverage the capacitance grows linearly with the deposition, increasing abruptly afterward. To understand the experimental data, we propose a model in which the linear response is attributed to isolated and agglomerated NPs. Initially, isolated NPs contribute to the capacitive response. **Beyond ~20%**

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coverage, shielded regions of the IDE due to agglomerated NP islands start to dominate. These interpretations are supported by Electron Microscopy and Atomic Force Microscopy. The proposed analysis allows improving the control of the concentration of NP deposited on surfaces systems with low coverage by monitoring the capacitance.

Keywords: magnetron sputter nanoparticle deposition, mass selected nanoparticle, nanoparticle thin films, in-situ capacitance measurement, silver, capacitance behavior modeling

1. Introduction

Nanostructuring paved the way to a plethora of exciting possibilities, from basic studies to new applications. These systems can present properties that differ sharply from their macroscopic scale counterpart or even show new and unexpected effects. Metallic nanoparticles (NP) and thin films, both examples of systems widely studied in this context, show optical [1, 2, 3], electrical [4] and catalytic [5] properties with great potential for new technological applications. Significant advances have been achieved in studying the electrical properties of metallic NP films. [6, 7] Most of these studies are based on samples deposited by atom deposition from the sputtering of metal targets. [8, 9] However, in this process, the nanostructure growth depends on the diffusion of metal atoms on the surface of the substrate. [10] In this context, the control, and modeling of the electrical properties of metallic NP thin films is crucial for the development and miniaturization of electronic devices and flexible electronics.

Electrical properties of metal films on surfaces obtained by the deposition of atoms are very complex because of the complicated interplay of different parameters like atom and island mobility on the surface, wettability and others [11, 12, 13, 8, 9]. Furthermore, films with metallic NPs as building blocks also present nanoscale and disorder effects that modify the electrical properties [14, 15]. J. E. Barborini *et al.* deposited Fe, Pd, Nb, W, and Mo clusters on interdigitated electrodes (IDEs), planar devices composed of metallic digits on

an insulating substrate, and performed DC electrical measurements during the film formation. They correlate the device resistivity evolution with the conduction path according to the formed film's mean thickness. They show that the resistivity decreases two orders of magnitude, due to the transition from 1D to 2D conductive path. The resistivity reaches a minimum, and then increases due to the formation of a 3D conductive path [14]. A. Sattar *et al.* describe how quantum conductance can lead to switching behavior in percolating nanoparticle films [15]. O. Kylián *et al.* report that the resistivity of Pt nanoclusters film on Si and glass decreases three orders of magnitude while the film thickness increases up to 50 nm, reaching $3 \times 10^{-3} \Omega \text{ cm}$ [10]. Recently, there were several reports on cluster assembled nanostructures that present memristive behavior. C. Minnai *et al.* reported switching behavior in Au cluster-assembled nanostructured films on glass substrates, which is attributed to the formation/destruction of conductive paths between particles [16]. M. Mirigliano *et al.* have reported the resistance evolution as a function of Au NP film thickness beyond the percolation limit and applied percolation theory to evaluate how the variation of nanoagregates connectivity influence the memristive effect [17]. Recently, A. Vahl *et al.* applied conducting atomic force microscopy to investigate *in situ* individual NPs alloys memristive effect and their structural degradation [18].

The vast majority of studies on electrical properties of NP films are based on DC measurements [14, 15, 19, 20, 21], that present no conductivity between low surface coverage and the percolation limit. However, many studies on metallic NPs deposited on a surface, exploring magnetic [22, 23], optical [3], and catalytic [24] properties, are carried out in a low concentration regime, where the interactions between NPs are negligible in order to preserve the intrinsic nanoscale properties of the NPs [25, 26, 27]. In this article, we report the experimental methods for *in situ* monitoring of Ag NP's deposition between the fingers of the IDEs via capacitance measurements. This technique allows the IDE electrical characterization from the very start of deposition up to the percolation threshold. To understand the experimental data, we propose a model based on how randomly distributed metallic NPs affect the electric field between IDE digits,

which can also be translated as variations in the capacitance. The methodology proposed here allows for better control and interpretation of metallic NP deposited on surfaces. These approaches can be further applied on other surfaces, such polymers. The incorporation of metallic NP into a polymer system has been exploited to tune sensor sensitivity and selectivity [28, 29, 30, 31] and suppress lithium dendrite growth in lithium metal batteries [32], for example. Nevertheless, so far, NP deposition on polymer has been achieved, leaving crucial parameters, like concentration, out of reach. In this sense, the NP deposition's electrical monitoring is essential to define NP concentration, which usually stays far below the percolation limit to better define the useful feature of these devices.

2. Materials and Methods

2.1. *In situ* capacitance monitoring of IDE during NP deposition

We fabricated NP using a gas aggregation source [33]. In this system, the erosion of a metal wire target produces a cloud of atoms. Collisions between sputtered atoms and cold Ar atoms promote NP formation. Figure 1(a) shows a scheme of the experimental setup used for the NP fabrication. A set of electrostatic lenses guides and focuses the positively charged NP beam onto the sample holder [34]. The set of lenses includes a Bessel box, allowing the selection of the NP mean size to be deposited on the sample holder. A fraction of the NPs produced are deflected to a time-of-flight mass spectrometer (TOF) that keeps track of the NP size distribution during the whole experiment. The major fraction of the NPs is deposited on the sample holder or on a current detector with a 200 mm² area that monitors the charged NP deposition rate. To estimate the area covered by NPs, we consider the spherical NP projection in circles of area A_{NP} . We estimate the NP covered area according to $\frac{A_{NP}}{A_{SENSOR}} \frac{t \times I}{e}$, in which $\frac{A_{NP}}{A_{SENSOR}}$ is the ratio between the NPs area and the current sensor area, t is the deposition time, e is the electron's charge and I is the NPs deposition current. The produced NP deposition current was monitored using a current detector connected to Keithley Series 6487 Picoammeters, which presented a mean value

of $I = 330$ pA. Besides, the NP mean diameter was monitored during the whole experiment using the TOF, which presented a mean diameter of ~ 3 nm.

Figure 1: (a) Experimental setup scheme of the atomic cluster source connected to a capacitance meter system. (i) Aggregation chamber where atoms are sputtered from a wire target and start aggregating in a low-temperature Ar atmosphere; (ii) electrostatic optics that guide, mass select and focus the NPs; (iii) time-of-flight mass spectrometer (TOF) for *in-situ* analysis of produced NPs size; (iv) 45 ° sample holder where IDE is mounted for *in-situ* capacitance monitoring; (v) neutralization filament to avoid charging effects on the sample; (vi) deposition chamber; (vii) capacitance meter setup. (b) Sample holder details to illustrate the NPs deposition on the IDE. Note that the IDE is rotated with respect to the sample holder position to better represent the deposition. (c) Although the NPs are deposited everywhere on the IDE, for clarity we show only the NPs deposited between adjacent digits. Sketch to illustrate the region between adjacent digits of the IDE to show (d) the parallel association of capacitors, (e) and the series capacitor after the sites (grey) being filled with nanoparticles.

To investigate the Ag NP film electrical properties, we have deposited the
85 produced NPs onto IDEs. Here, we used gold IDEs on glass, comprising 30
pairs of digits with 3 mm length, 200 nm height, 40 μm width, and spaced 40
 μm each other, fabricated at the Microfabrication Laboratory, National Center
for Research in Energy and Materials, Brazil. We performed capacitance mea-
surements to analyze *in situ* the evolution of the electrical properties of IDEs

90 during Ag NP deposition, as schematically shown in figure 1(b). Measuring *in situ* avoids NP oxidation, which is an important issue when using such small NPs [35]. The produced NPs are randomly deposited on the whole IDE, and the NPs deposited on the IDE digits do not modify the overall electrical properties. However, the NPs deposited between adjacent digits, equivalent to half of the
 95 total IDE area, do modify the electrical response, as illustrated in figure 1(c). We perform capacitance measurements using a homemade setup, described in detail elsewhere [36]. Briefly, a sinusoidal voltage of 1 V amplitude at 1 kHz is applied to one comb of digits of the IDE [36]. The current from the pick-up electrode is amplified using an operational amplifier in a differential configuration.
 100 A lock-in system measures the output voltage and the phase shift between input and output signals in 0.5 s intervals. We interpret the measurements using an equivalent circuit composed of a parallel association of capacitive and resistive components [36] The metal NP deposition between the IDEs digits modifies the device geometry. For instance, considering that the region between adjacent dig-
 105 its can be approximated to a parallel association of capacitors, the nanoparticle deposition decreases the gap of the capacitors, which is equivalent to having an series association of capacitors, as shown in Figure 1 (d), and (e), respectively. Consequently, increasing the total capacitance.

2.2. *Ex situ morphology investigation*

110 We investigated the coverage and the topography of the NP film deposited on the IDE to interpret the electrical behavior observed. After the NP deposition, we analyzed the topography of the region between the IDE's digits using Atomic Force Microscopy (AFM), in a BRUKER Dimension ICON instrument, using a rectangular shaped silicon tip, 42 Nm^{-1} spring constant and 330 kHz free oscillation in tapping mode. Complementary information about the NP size evolution
 115 is obtained from Transmission Electron Microscopy (TEM) experiments. The NP size distribution and covered area on a surface were investigated on samples produced by the deposition of Ag NP for different deposition times on Ultrathin Carbon Film Supported by a Lacey Carbon Film on 400 Mesh Copper TEM

120 grids. These grids were analyzed using a Jeol 2100F field emission gun TEM at
Electron Microscopy Laboratory, National Center for Research in Energy and
Materials, Brazil.

3. Results

3.1. Capacitance monitoring of silver nanoparticle deposition

125 The capacitance evolution, as a function of the fraction of area covered
by the NPs, from the very beginning up to 50% coverage, is shown in figure
2. At the beginning of the deposition, the measured capacitance value was
 $C_{\text{IDE}} = 10.25$ pF, corresponding to the bare IDE in vacuum [37, 38]. A mono-
tonic increase of capacitance following the NP coverage is observed even during
130 the early stages of the deposition, demonstrating higher sensitivity than what is
usually seen in DC measurements of resistivity [14, 9]. Besides, figure 2 allows
us to infer that the capacitance measurements presents two growth regimes: an
initial linear growth for the first 20% of the covered area, which becomes super-
linear after 20% of covered area. The measurement was stopped after one hour
of deposition, which was equivalent to 50% of the estimated covered area.

Figure 2: IDE capacitance variation as a function of the covered area during the deposition of 3 nm silver NPs.

135

Figure 3: (a) $10\ \mu\text{m} \times 10\ \mu\text{m}$ and (b) $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM micrograph between IDE digits after the NP deposition. Note that the holes are related to incompletely filled NP layers.

3.2. Morphological investigation of silver nanoparticle on surfaces

To analyze the topography between adjacent digits, we performed an AFM analysis. Figure 3 shows an AFM micrograph of the IDE used to obtain the capacitance behavior shown in figure 2. As shown in figure 3(a), the deposited NPs form an almost continuous thin film, with some incompletely filled islands. The mean height measurement in the depression regions is (4.0 ± 0.5) nm, which is equivalent to the NP diameter. Figure 3(b) was obtained where the NPs form a seemingly continuous film. We can observe that the NPs do not form an ordered packed film as assumed for the covered area estimation, but they are randomly distributed on the surface. The micrograph also shows that the NPs start to agglomerate on top of the unfilled layer of previously deposited NPs.

Figures 4(a-c) present TEM micrographs of Ag NPs for 1.5%, 5%, and 11% covered area, respectively. We observe that an increasing percentage of the

Figure 4: TEM micrographs of Ag NPs: (a) 1.5% covered area, (b) 5% covered area, (c) 11% covered area. We can observe that the NPs coalesced on the grid and increased their diameter with the covered area. Size distribution for (d) 1.5% , (e) 5% and (f) 11% covered area. The red curve is the time-of-flight size distribution during the sample preparation, which presents 3.2 nm for the NPs mean diameter.

covered area also increases the NP diameter due to coalescence. The size distribution obtained for these micrographs are compared with the time-of-flight size distribution, shown in graphs 4(d-f). We can see that for 1.5% covered area, the NP size distribution derived from the TEM analysis coincides with the TOF size distribution obtained during deposition (figure 4 (d)). Increasing the percentage of covered area shifts the NPs mean size and broadens the distribution towards bigger NPs, as shown in figures 4(e) and (f).

4. Model

4.1. Capacitance evolution during silver nanoparticle deposition

The capacitance monitoring during the 3 nm Ag NPs deposition on a bare IDE shows a capacitance growth profile with the covered area, figure 2. In contrast to DC measurements, the capacitance measurements starts to increase from the very beginning of the deposition, which corresponds to the contribution of isolated NPs to the device capacitance. The variation in capacitance due to

the NPs occurs because of the change in the electric field they cause when deposited in the area between digits. The IDE capacitance can be represented
165 by an equivalent circuit of parallel capacitors that describe the contribution from different parts of the IDE to the total capacitance. For example, one capacitor can take into account the contribution from the top of the digits, and another the region between digits, where the field is parallel to the IDE substrate. Different parallel capacitors then describe this last region. In this
170 sense, deposited NPs only affect one of these capacitors, representing a fraction of the capacitance due to the region between digits and close to the substrate surface. All other contributions remain constant during the experiment. In this sense we can write the total capacitance as a function of the covered area A by $C_{\text{total}}(A) = C(A) + C'_0$ where $C(A)$ was the capacitance due to the NP
175 deposition and C'_0 the part that remained constant throughout the deposition.

To interpret the observed capacitance behavior, we propose a model based on a simulation of the evolution of the capacitance during the random filling of a rectangular mesh grid that represents the area between the IDE digits with NPs, as illustrated in figure 5, where grid positions are filled randomly to mimic
180 NP deposition over time. The digit spacing S and length L is divided in squares of side $\Delta S = \frac{S}{n}$ and $\Delta L = \frac{L}{m}$, respectively. To keep the device aspect ratio of the region between digits, we use $m = 75n$. Each cell is addressed with a pair of indices, (i, j) , with $i \in [1, n]$ and $j \in [1, m]$ for the spacing (S) and length (L) positions, respectively. Each column j is associated with a capacitor C_j of
185 parallel plates, as depicted in figure 5. The gap between digits corresponds to the distance between the plates of each C_j capacitor. The capacitance of this device is thus equivalent to an array of parallel capacitors C_j , i.e., $C(A) = \sum_{j=1}^m C_j(A)$. Therefore, $C(A = 0\%) = C_0$, is the initial value of this capacitance in vacuum, before any deposition. Let a particle be introduced at row i and column j in the
190 grid. When i is the first or last available space in column j ($i = 1$ or $i = n$), the capacitance C_j changes as if the capacitor's gap was reduced by one grid space ΔS . If instead the particle is introduced at an intermediate space $1 < i < n$, the capacitance C_j becomes the series association of two parallel capacitors with

gaps $(i-1)\Delta S$ and $(n-i)\Delta S$. Note that the total sum of the gaps is also reduced
 195 by one grid space like before, but now it created two capacitors. In figure 5, red
 squares illustrate sites filled with NPs.

We must also take into account that NPs agglomerate and that they also
 touch the digits, as illustrated in figure 5. In these situations, empty sites can
 be shielded from the electric field by sites occupied by NPs. The dark blue
 200 squares in figure 5 illustrate situations in which empty sites are shielded by
 agglomerations of NPs, with or without contact with the digits. In the model
 proposed for $C(A)$, groups of adjacent particles with at least one connection
 to a digit will shield all empty sites between any constituent particles and the
 nearest wall. Shielded sites contribute to $C(A)$ as if they were occupied.

Figure 5: Schematic of the rectangular mesh depicting regions with (right-hand side) and
 without (left-hand side) agglomeration of NPs. Light blue squares are empty sites; red squares
 are filled with NPs and dark blue squares are the shielded positions. The simulations discussed
 in the text were performed for larger meshes ($S = \Delta S n$ with $n = 50$).

205 In our experiment, it is not possible to separate $C(A)$ from the constant
 capacitance value, C'_0 . As $C(A)$ is proportional to the initial value $C(A = 0\%) =$
 C_0 , we can rewrite it as $C(A) = k(A)C_0$. So, we adjusted the proposed model
 for $C(A)$ to the experimental curve considering that $C_{exp}(A) = k(A)C_0 + C'_0$
 and find the values for C_0 and C'_0 to evaluate the total capacitance as a function
 210 of A using our proposed model.

5. Discussion

In the previous section, we have proposed a model to calculate the evolution of the conductance as a function of the covered area. For the calculations, we used a mesh with $n = 50$. We also performed the calculations for a bigger mesh, which increases the computation cost but yields compatible results. Figure 6(a) shows the experimental data, the capacitance simulated without considering the agglomeration of NPs, the simulated considering shielded regions due to agglomerated NPs, and the linearly adjusted region used to normalize both simulations to the experimental data. Figure 6(b) presents the number of agglomerations and effective coverage as a function of the covered area. The former is for the number of isolated NPs and the number of groups of NPs that are considered agglomerations in our models. After sorting a position in the matrix to be filled, our method analyzes the whole matrix and counts the number of agglomerations in each iteration. The number of agglomerations increases until reaching approximately 20% coverage. Beyond 20% coverage, new deposited NP falls on or connect pre-formed agglomerations, decreasing the number of agglomerations, leading to the bell-like dependence of the number of agglomerations as a function of the covered area seeing in figure 6(b). The effective coverage refers to the sum of sites in the grid containing an NP or shielded by an agglomeration.

We see in figure 6(a) that experimental and simulated results are in good agreement when the linear portion of the curve is considered (up to 20% of coverage). It is important to remark that the model without agglomeration is, in fact, a linear capacitance function of the covered area up to 50% coverage, and therefore, it is incapable of describing the non-linear behavior observed for coverages higher than $\sim 20\%$. Moreover, figure 6(b) showed that the number of isolated and agglomerated NPs grows until $\sim 20\%$ of coverage and then goes down. Also, the % effective coverage was linear until $\sim 20\%$ of the covered area and started to increase rapidly. This behavior indicates that initially, the IDE's capacitance can be described by the effects of isolated NPs.

From 20% coverage onwards, the capacitance begins to be dominated by the

Figure 6: (a) Experimental and simulated values of IDE capacitance during NPs deposition. (b) Left: the sum of the number of isolated NPs and the number of agglomerated NPs; right: % of occupied and shielded positions on the grid. The dashed line describes the % covered area, also associated with right-hand axis.

existence of clusters of NPs that shield regions of the IDE. This can be verified in figure 6(a), where the simulation with shielded sites from agglomerated NPs (green curve) follows the experimental data up to $\sim 45\%$ coverage. Besides, from $\sim 20\%$ coverage, the number of agglomerations decreases, indicating that isolated NPs as well as agglomerations **start to touch, being considered as coalescence**. Also from this point on, the % of effective coverage is no longer linear with the % of the covered area, but grows faster. This result indicates that the contribution of shielded areas, due to NP agglomeration, must be considered in

order to understand the IDE capacitance behavior from 20% coverage.

250 Above 45% coverage, the IDE capacitance in our model saturates, not correctly representing the experimental data. This can be related to the percolation threshold, which adds a resistive component to the device. According to the literature, the percolation occurs for 40% coverage in a square matrix with next-nearest neighbour conductance, from this point on our model is no longer
255 adequate [39]. Besides, the % of effective coverage also saturates (occupied and shielded positions on the grid). We recall the literature showing a measurable conductive component in electrical transport for over 45% coverage [40], which must contribute to the measurement of our IDE electrical behavior.

We furthermore note here that our simple model correctly reproduces not
260 only the overall trend but can even quantitatively describe the variations in capacitance despite its simplifications. From the AFM image in Figure 3 we can deduce that three-dimensional growth is non-negligible; we have, however, tested that permitting a second layer of deposited NPs in the model has only minor effects. This is comprehensible as additional layers only slightly re-scale
265 the abscissa of Fig. 6.

6. Conclusions

Surface deposition of metal NPs for numerous studies, on the one hand, relies on controlling the low concentration of NP on the substrate. On the other hand, works on the electrical properties of films of NPs usually investigate films
270 that are close to or above the percolation limit, where electric transport is predominately resistive. We have focused in our study on the evolution of the sample capacitance from the very beginning of the NP deposition up to the percolation limit. The observed variation in capacitance can be divided into two regimes, a linear one between 0% and $\sim 20\%$ coverage, and a non-linear one
275 for values above $\sim 20\%$. To interpret these results, we propose a simple model based on the occupation of sites between digits. The model takes into account how agglomeration of NPs leads to the formation of shielded sites that affect the

electric field between electrodes and the capacitance consequently. This model shows that the first capacitance regime is dominated by isolated and agglomerated NPs. Above $\sim 20\%$ coverage, the capacitance starts having contributions of shielded regions between the electrodes due to agglomerated NP islands, leading to a super-linear capacitance increase. TEM and AFM micrographs support our interpretations. The proposed model and electrical behavior analysis open possibilities to control the concentration of NP deposited on surfaces for optical, magnetic, and catalytic studies. Besides, our work contributes to the development and miniaturization of electronic devices and flexible electronics based on IDEs with NPs film. It can also be extended to the deposition of wet-chemically synthesized NPs, facilitating the comprehension of several phenomena and effects caused by NP introduction in a variety of applications in several knowledge areas.

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