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NONLINEAR CONDUCTION IN PLATINUM NANOPARTICLE FILMS

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Platinum nanoparticles with the size between (25-150)nm have been deposited on a SiO_2/Si substrate by laser ablation. Roughly estimated, the particle distribution deviates from lognormal distribution at larger particle size. Electrical measurements on nanoparticle films with different surface coverage revealed that the films start conducting at a given threshold. As expected, ohmic I-V characteristics were found in all investigated structures. However, below a voltage threshold, a transition from linear to pronounced nonlinear behaviour was observed in the samples with a higher surface coverage. Tunneling mechanism between the metal islands partially embedded into substrate is proposed as a source of nonlinearity. It points out to the interaction between nanoparticles film and the substrate, a conjecture strongly supported by the observation of some Pt_3Si lines in the x-ray diffractogram. Other possible causes of nonlinear conduction mechanisms are heuristically discussed.

1. INTRODUCTION

“Ultrafine metal particles”, to name the pioneering paper of Granqvist and Burhman [1], have been for a long time investigated for their extremely useful properties in “classical” applications such as catalysis, powder metallurgy, etc. [2]. In the last decade, a plethora of new applications has been intensively searched especially for the domains where the role of the nanoparticles is highly functionalized. For instance, metallic nanoparticles are envisioned as possible intermediate connections between macroscopic contacts (pads) and active molecules in molecular electronics. Recently, Gittins et al. [3] demonstrated that metallic nanoparticles (gold) can be used to realize nanoscale electronic switches operating with less than 30 electrons, while Thelander et al. [4] showed that gold nanoparticles connected to the carbon nanotubes feature Coulomb blockade effects at 200K. Moreover, Coulomb blockade was observed in silver nanoparticle films deposited on Au substrate even at room temperature [5]. Assemblies of nanoparticles are investigated as potential candidate for “less conventional forms of computing” [6], whereas selforganized nano-particles can also act as memory elements in “nanocomputers”. In fact, the examples of functionalized applicability of the nanoparticles are practically countless. What is rather common to all these applications is how these systems are conducting charge. Moreover, the electrical properties of the nanoparticle films could be of some relevance even for the catalysis process for it has been recently shown by Somorjai [7] that a platinum nanoarray is 20-30 times more active than a platinum foil. The explanation was found in the Pt/SiO_2 interface which is of paramount importance in the catalysis. Also in this case, how this system is conducting charge could be a key issue in understanding its unusual properties.

During the electrical characterization of the platinum nanoparticle films on SiO_2/Si substrate, we have observed nonlinear effects in the I-V characteristics. The purpose of this contribution is to present these preliminary results and to offer some possible explanations.

2. EXPERIMENTS

Platinum nanoparticles were deposited on a SiO_2/Si substrate by laser ablation. The method is similar to the conventional pulsed laser deposition (PLD). The interaction of a focused laser beam with a solid target causes evaporation and plasma formation. Evaporants form a plume consisting of various species including atoms, molecules, ions, electrons, clusters, etc.. After the laser irradiation, the plume rapidly expands forward along the target normal. The particles are deposited in general on a substrate placed at 3-10 cm from the target. The experimental setup consists of a reaction chamber with associated system for laser beam focusing, vacuum pumps, etc.. Base pressure of 1.5×10^{-5}Torr was routinely achieved. The substrate was placed at 6 cm distance from the target (platinum 99.9%) which was uniformly irradiated in order to avoid drilling. The Nd:YAG laser delivers pulses of 125 mJ/5 ns (full width at half maximum)/355 nm/10 Hz. The beam was focused onto the target with a lens defining a fluence of 14.8 J/cm^2. The particles deposition has been made on different substrates (NN6-NN15) of SiO_2/Si(111), with a variable number of pulses.

To estimate the particle dimension and shape, some of the films were investigated by atomic force microscopy(AFM) in both contact and tapping mode. X-ray diffraction has also been used to investigate the structure of the nanoparticles and possible differences between differently processed samples. Conduction measurements have been done with a simple four probe system. All measurement were performed at room temperature.

3. AFM INVESTIGATIONS

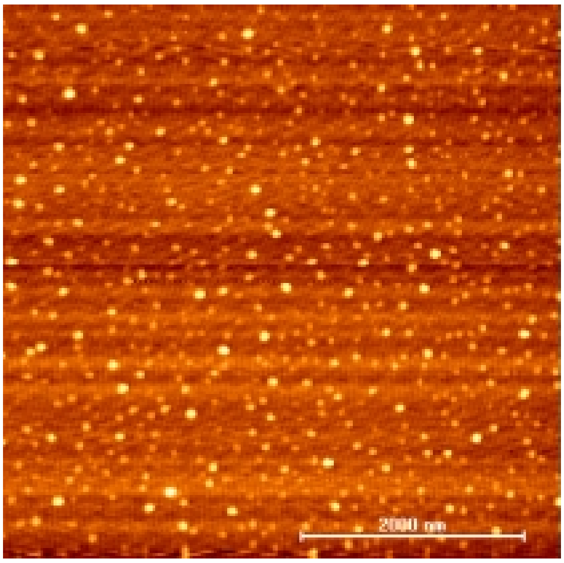

Fig. 1 - AFM image of the laser ablation grown platinum nanoparticles on SiO_2/Si substrate

AFM investigations revealed the presence of platinum nanoparticles on the SiO_2/Si substrate (Fig. 1). Their size was distributed between 25 nm and 150 nm. On a relatively small AFM scanned area, the distribution of the particles was roughly estimated. Although the distribution can be very roughly described by a lognormal distribution, a better fit was obtained by superposition of two lognormal distributions. The maximum of the distribution has been located around 50nm. Although our distribution seems to be somehow unusual, we note, however, that this is not unique at all for a "composed" distribution has also been reported for platinum nanoparticles grown by other methods [8].

Moreover, deviations from a lognormal distribution have been reported by Granqvist and Buhrman [1] for particles of larger size which feature *crystal habit*. Indeed, we have observed such a tendency in the AFM images of the larger particles.

4. NONLINEAR EFFECTS IN I-V CHARACTERISTICS

I-V characteristics of the nanoparticle films were determined using a four-probe system. No current flow was observed in the sample NN6 with the smallest nanoparticle coverage, while the second sample(NN7) was conducting. Its I-V characteristic, along with those of the samples NN8-NN10, are shown in Fig. 2.

The samples NN7-NN9 feature ohmic conduction in almost the whole current range, with some small deviations at lower currents. In the linear region, the film conductivity increases with the quantity of the deposited material or the surface occupation. A larger increase is observed between the samples NN7 and NN8, an observation which supports the idea that, for the given ablation conditions, there is a conduction threshold between NN6 and NN7. Such a behaviour is reminiscent of percolative systems [9]-[12]. Our results, although incomplete, suggest the existence of a conduction threshold, but our effort to evidence this percolation threshold was unsuccessful to date. A transition from ohmic conduction to a superlinear behaviour is observed in the I-V characteristic of the film NN10, under about 300µV. The I-V characteristics of the films with a higher surface coverage are presented in figure 3.

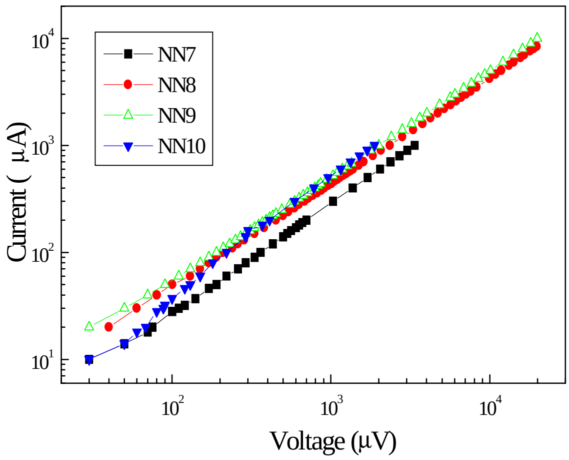

Fig. 2 - I-V characteristics of the samples NN7– NN10

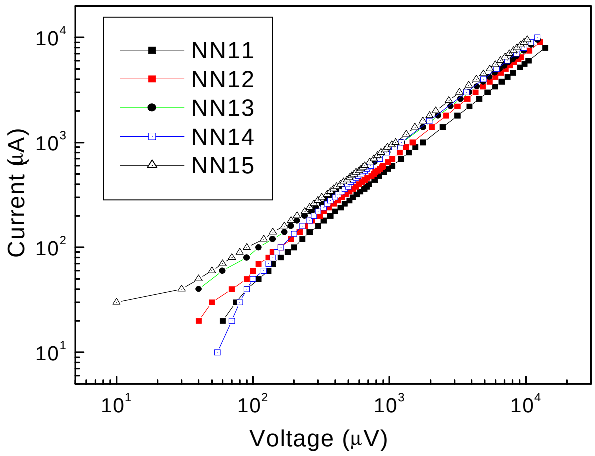

Fig. 3 - I-V characteristics of the samples NN11-NN15 with a higher surface occupation

At small currents, nonlinear effects were observed in all samples NN11-NN15. Except for the sample NN14, there is a clear transition from a superlinear mechanism to a sublinear one. In the nonlinear region of the I-V characteristic of the sample NN14, till about 600µV, the experimental results are well described by a equation of the form I~exp(V/a), where I is the current, V is the voltage (in mV) and a=2.72. The Ohm's law is valid beyond V=600µV. For V< 600µV, all I-V characteristics are well described by such an equation.

5. WHERE DOES THE NONLINEARITY COME FROM? - AN HEURISTIC APPROACH

Deviations from the Ohm's law are always interesting *per se* for sometimes they are the expression of some subtle microscopic conduction mechanisms. Adopting an heuristic approach to answer where the nonlinearity comes from, two difficulties were encountered in interpreting the experimental data:

1. the samples with the smaller coverage are almost ohmic in the whole voltage range, while the samples with higher coverage are not;
2. we have nonlinear-linear transition instead of the most usual Ohmic-nonlinear transition.

By analogy with what happens in the percolative systems [9]-[12], one can suppose that in our nanoparticle films there are dual conduction mechanisms. Henceforth, one has to consider that different conduction mechanisms are at work in our samples. In fact, it is well-known that both metallic and tunneling are the dominant conduction mechanisms in metal-insulator systems above the percolation threshold; moreover, the conductivity is dictated by metallic conduction while its fluctuations are dominated by tunneling between particles [12].

The fact that deviation from Ohm's law occurs once the structure of the film becomes more "compact" is an indication that some structural modifications are involved. In a seminal paper on discontinuous metal films, Neugebauer and Webb predicted that "the conductance of the thick films changes more rapidly with the applied voltage than the thinner ones" [13]. The reason is that the space between the particles (gap width) decreases and, consequently, the interparticles field increases. The effect was observed in discontinuous platinum films [14] wherein the thermionic emission was disclosed off for it is insensitive to the gap width, the remaining being the tunneling which is very sensitive to the distance between metallic islands. One can thus suppose that although the dominant conduction mechanism in the ohmic region is the metallic conduction, there is always a tunneling component. It can manifest stronger at small voltages. Therefore, in the samples NN7-NN9, the metallic conduction is dominating in the whole voltage range, while in NN10-NN15 it dominates above a conduction threshold. The problem at stakes is why the metallic conduction does not extent to lower voltage as would be naturally for the samples with higher coverage?

A possible answer can be found if one takes into consideration that for the films with the higher thickness the nanoparticles interact with the substrate. If, for instance, they are embedded in the SiO_2 matrix, tunneling can take place in the substrate, hence with a thin SiO_2 dielectric layer between the metallic islands. This situation is encountered in discontinuous metallic films [14],[15]. It is worth mentioning that in the less covered samples, tunneling takes place in the air and this seems to be the main difference between the two categories of samples.

The role of the substrate can be important even for a monolayer, as reported recently by Otten et al. [16] which investigated charge transport mechanisms in a system of PbS nanoparticles deposited on either GaAs or GaAs topped with a SiN_x layer. A close look at their results shows that in the more conductive substrate the current (I) features a V^2 dependence, which is a clear signature of the space charge limited currents [17]. In our case, the role of the substrate comes to the fore by X-ray diffraction analysis. Figure 4 shows comparatively the X-ray diffractograms of the samples NN14 and NN15. The X-ray diffraction experiments were done with a Mo anticathod tube; the following parameters have been used: V = 40kV, I = 20mA, with a 2θ step ranging from 0.02^o to 0.05^o and the integration time of 10 seconds.

From fig. 4 one can observe that for the sample NN14 both platinum lines, at (111) and (200), are located above two very broad peaks which correspond to a platinum amorphous phase. The deposited material on NN15 sample is almost entirely amorphous. Superposed on this large "amorphous" peak are some peaks which are associated with a crystalline state of Pt_3Si. A weak and very extended peak is also observed at about 21.11^O in NN14. It can be assigned to an amorphous state of Pt_3Si.

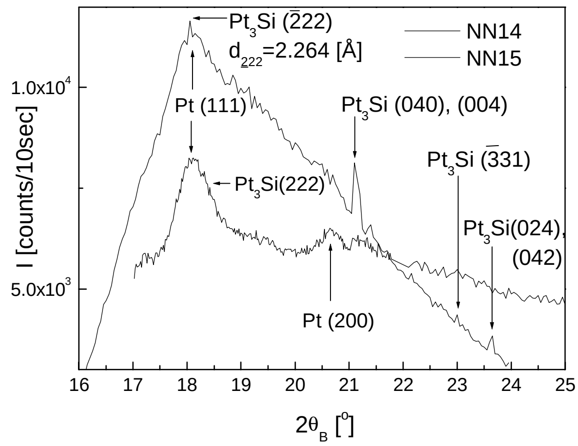

Fig. 4 - X-ray diffractograms of the samples NN14 and NN15. For NN15 the spectrum was obtained with a K_β filter.

The above presented results do not explain the differences between the samples in the nonlinear region, they only support the hypothesis that deposited material interacts with the substrate.

Although the occurrence of Pt_3Si can be highly controversial, it is beyond the purpose of this work to give some clues of how this silicide film would grow. The presence of $PtSi_3$, if any, would favor the formation of some conducting pathways between nanoparticles and the substrate. The shape of the I-V curves also suggests that a possible "parasitic" conduction mechanism would be involved. We are thinking of a kind of Schottky parasitic contact.

Finally, we just mention that another fascinating mechanism which could be invoked is the so-called Coulomb blockade. For a tunnel junction containing metal particles in a oxide layer, Shekhter[18] showed that when the "Coulomb energy is small in comparison with the temperature […] Ohm's law is valid over the entire range of voltage". Recently, nonlinear effects due to Coulomb blockade in nanoparticle films have been reported [5],[19],[20]. In comparison with some existing data in literature, our measurements are far less refined to draw any conclusion in this respect.

CONCLUSIONS

Laser ablation technique has been used to grow platinum nanoparticles on SiO_2/Si substrates. The particle size was between (25-150)nm, while its distribution deviates from a lognormal one for larger sizes. Electrical conduction measurements indicate that the prepared samples are above a possible percolation threshold. Only ohmic conduction was found in the samples with smaller coverage. It was attributed to the metallic conduction. The I-V characteristics of the samples with higher coverage featured nonlinear effects under a voltage threshold. These effects were tentatively attributed to the tunneling between metal islands which are partially embedded into the SiO_2 matrix. That the substrate is involved in the conduction has been proven by X-ray diffraction. The results presented here warrant for further investigations.

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