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NONEQUILIBRIUM 1/F NOISE IN PLATINUM NANOPARTICLE FILMS

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1/f noise spectra have been observed in platinum nanoparticle films deposited on SiO_2/Si substrates by laser ablation. Although all noise measurements were done in the linear region of the I-V characteristics, both equilibrium (ohmic) and nonequilibrium (nonohmic) behavior was observed in the dependence of the noise intensity on voltage (V). The nonequilibrium 1/f noise was found in some samples of smaller conductivity (small coverage). The sample with the smallest noise intensity features strong sublinear ($V^{0.2\text{-}0.37}$) nonequilibrium 1/f noise for voltages V<0.5V, while for V>0.5V the noise intensity is superliniar ($V^{3.2}$). In the (20-300)K temperature range, the film resistance follows a $T^{-1/4}$ dependence, specific to Mott's phonon-assisted variable range hopping conduction.

1. INTRODUCTION

Ultrafine particles can interact either with the substrate they are sitting on [1],[2] and other environmental factors such as adsorbed atoms/molecules. Such interactions can be very detrimental for highly functionalized applications in nano and molecular electronics. For instance, in a classical structure of single-electron transistor (SET), the island-substrate interaction can be very noisy. Such effects were also observed in nonconventional structure of SET consisting of carbon nanotubes on SiO_2 substrate [3]. When the nanotube is suspended, the structure is much less noisy. If the "classical" island is replaced by nanoparticles, the Coulomb blockade is observed at a higher temperature (200K), as in the case of gold nanoparticles connected to the carbon nanotubes terminals [4], while for silver nanoparticle films deposited on Au substrate, the effect was observed even at room temperature [5]. This advantage can be seriously counterbalanced by the noise associated either with the granular structure of the island and its nanoparticles interaction with the environment (e.g.: substrate, adsorbates, etc.). Therefore, identifying the sources and the nature of the noise phenomena in small dimensional structures seems to be a *sine qua non* condition for further development in the field of nanoscience.

On the other hand, as reported recently [6],[7], noise investigations in nanoparticle films are interesting *per se* for they are able to evidence subtle microscopic conduction mechanisms in such discontinuous structures. For instance, noise measurements performed by Otten et al.[6] on PbS nanoparticle films, grown on both GaAs and SiN_x substrates, evidenced spectra of the $1/f^n$ form, with the frequency exponent n=1/2 and/or n=3/2. These spectra are specific to the diffusion of the electrons between nanoparticles which takes place either at the surface and/or bulk substrate. Hence, the shape of the noise spectrum is very useful to identify the nature of the transport processes between nanoparticles. In particular, in this case, one can deduce that the substrate is involved in the conduction. Fundamental hypothesis have been also checked by noise measurements**,** as recently done by Hoel et al.[7] who found that noise measurements on WO_3 are in concordance with the fluctuation-dissipation theorem**.**

We have done noise measurements on platinum nanoparticle films grown on SiO_2/Si substrate by laser ablation. Although the measurements have been performed in the linear region of the I-V characteristics in all cases, both equilibrium and nonequilibrium (driven) 1/f noise was found. It points out to the presence of

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both linear and nonlinear conduction mechanisms in our samples. In this contribution we present these results, their possible impact on some old perennial questions in the field of low frequency noise and investigate the possible causes for such a behavior.

2. EXPERIMENTS

Platinum nanoparticles were deposited on SiO_2/Si substrates by laser ablation. A variable number of laser pulses has been used to obtain different surface coverage. Some of the films were investigated by atomic force microscopy (AFM) and X-ray diffraction. Conduction and noise measurements have been carried out on samples with different coverage. To this purpose, silver paint contacts, located few mm apart, were deposited on the films surface. I-V characteristics of the nanoparticle films were determined using an automatically data acquisition system, for voltage ranging from hundreds of microvolts to about 20V. For noise measurement, batteries in series with a low noise resistor were used to inject current into the film terminals. The voltage developed across the film terminals was amplified and Fourier transformed with an SR 780 noise analyzer. All noise measurements were done in the ohmic region of the I-V characteristics, at room temperature. To look for the conduction mechanism, conduction measurements were done in the (8-300)K temperature range on one of the samples (NN9).

3. RESULTS AND DISCUSSION

AFM investigations revealed the presence of platinum particles on the SiO_2/Si substrate [8]. Their size varies between 25nm and 150 nm. Roughly determined, the particle distribution was a deformed lognormal one at larger sizes, with a maximum at about 50nm.

Figure 1 shows the I-V characteristics of some nanoparticle films grown on SiO_2 of different thickness: 500nm (samples 1, 4 and 6) and 120nm (samples 8 and 9). For voltages lower than about 10mV, the I-V characteristics are nonlinear. Above this voltage threshold till 20V, the characteristics are linear. Note that the conduction properties are almost similar in the sample pairs 1/8 and 4/6. Such nonlinear effects were also observed in all samples with higher coverage (NN8-NN15).

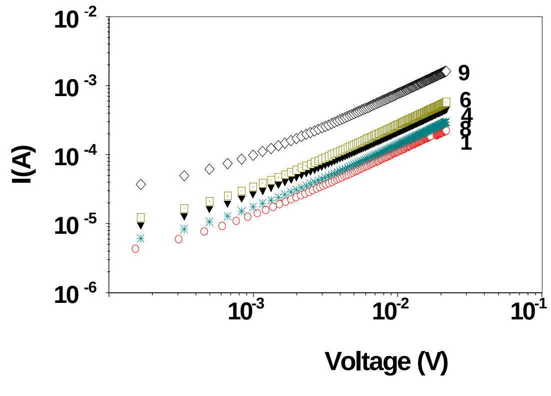

Fig. 1– I-V characteristics of some nanoparticle films at low voltages; the samples 1, 4 and 6 were grown on a 500nm thick SiO_2, while samples 8 si 9 were deposited on a 120nm thick SiO_2.

The interpretation of the conduction mechanism is very challenging because usually, in most of the cases, the conduction is linear at small voltages and nonlinear at higher voltages. Hence, there is a transition from metallic conduction to a nonlinear mechanism, most probable tunneling or hopping. In the case of our films, this hypothesis is supported by the fact that the nonlinear region of the I-V characteristics is well described by an equation of the form $I \sim \exp(V/n)$, where I is the current, V is the voltage and n is a parameter. On the other side, the nonlinear region of the I-V characteristics can be well described by a $I \sim V^{1/2}$ law. For PbS nanoparticles grown on the SiN_x/GaAs substrates, Otten et al. [6] reported I-V characteristics of the

$I \sim V^{1/2}$ form. From other considerations, they deduced that conduction takes place in the SiN_x substrate or at its surface, therefore the $I \sim V^{1/2}$ law can be dictated by the substrate participation. Hence, one can suppose that also in our case the SiO_2 substrate could be involved in the conduction process.
By analogy with what happens in metal-insulator composite [9],[10], these observations suggest the presence of a dual conduction mechanism. Therefore, while conductivity in the ohmic region is controlled by metallic conduction, its fluctuation can be dominated by tunneling or by other conduction phenomena (e.g.: hopping). This situation has to be reflected in noise.

1/f-like noise was found in all samples (nine), with the frequency exponent (m) varying between 0.7 and 1.4. Voss and Clarke [11] have found that 1/f noise exists in the thermal noise, hence 1/f noise is an equilibrium phenomenon. Consequently, a current trough the sample does is not the source of the noise, as believed for a long time, it is only necessary to probe the presence of the equilibrium 1/f noise. This situation is reflected in the Hooge's [12] heuristic formula, which is also very useful to quantitatively evaluate the noisiness or the so-called 1/f noise parameter, γ, of a linear physical system from:

$$\frac{S_V}{V^2} = \frac{\gamma}{Nf}, \tag{1}$$

where S_V is the noise spectral density, measured at a frequency f; V is the voltage which develops across the terminals of a linear resistor when a current is injected in it; N is either the total number of electron or atoms in the investigated sample (still in dispute). A dependence $S_V \sim V^2$ mirrors the validity of the Ohm's law in noise and the current flow is revealing only the presence of the otherwise equilibrium 1/f noise. Any deviation from the quadratic V^2 law is the signature of a nonequilibrium, current driven noise mechanism.

Assuming that for all nanoparticle films $S_V \sim V^2$, the relative noise intensity (S_V/V^2) was calculated, and its dependence on the film conductance is presented in Fig. 2. Apparently, for smaller conductance (coverage), the general tendency for the noise intensity is to decrease with the sample conductance. After a minimum (sample NN9), the noise intensity not only "recovers" but also experiences a slight increase for higher conductance.

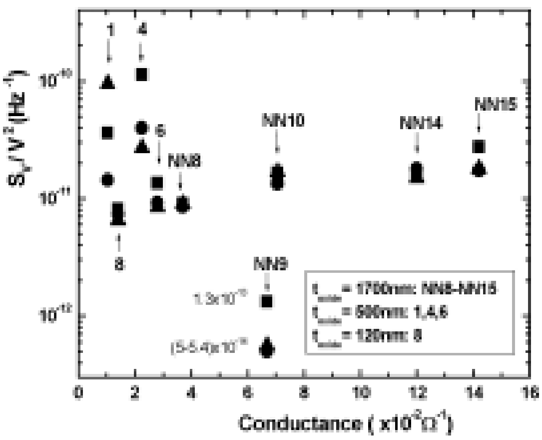

Fig. 2 - Dependence of S_V/V^2, at f=10Hz, on film conductance. For each sample, the triangle, square and dot represent the noise data for three different currents.

However, the scattering of the experimental data for the samples 1, 4 and NN9 obviously impedes on such a simple interpretation. Indeed, as depicted in Fig. 3, samples 1 and 4 feature a strong nonlinear noise ($S_V \sim V^n$, n<1), while for the samples 6 and 8 the noise intensity not only decreases but also shows a pronounced tendency towards a linear behaviour ($S_V \sim V^2$). Except for NN9, this tendency is also maintained for all samples with higher coverage. Although measured, as all films, in the ohmic region of the I-V characteristics, the deviation of the noise intensity from the Ohm's law is the evidence that the noise mechanism in the samples 1, 4 and NN9 is strongly nonlinear. Variable voltage exponents have been also recently reported by Chiteme et al. [13] for cellular percolation systems. It results that the procedure of normalization is not suitable for the samples 1, 4 and NN9. Consequently, if the data for these samples are ignored in Fig. 2, one observes that the noise slowly increases with the film conductance, which is at odds with the Hooge's 1/N law, for one expects that the total number N of the carriers in the sample to increase with the coverage. However, these results are in accordance with the "minimum noise" level defined by Fleetwood and Giordano [14]. For a large number and diversity of metal films, they have found a minimum noise level whose intensity increases with the film conductivity. In close connection with their data is also the behavior of some sample "pairs" (1/8, 8/4, 4/6, NN9/NN10) whose conductance is slightly different while the noise differs by a factor of 10, at least. Therefore, such an intriguing behavior, often encountered in metallic films [14], can be explained by the fact that even in a linear nanoparticle film, the noise mechanism can be strongly nonlinear and of nonequilibrium nature. Although other causes cannot be excluded, the nonlinearity and, hence, improper normalization could be a cause for such a large difference in the noise intensity in nominally identical samples.

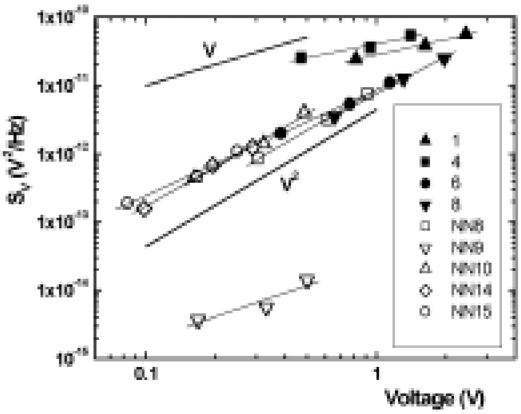

Fig. 3 - S_V/V^2 vs. V for all Pt nanoparticle films investigated by noise measurements; f=10Hz

Since in these samples, the noise is less voltage dependent, hence less dependent on the interparticle potential barrier, the noise could be considerably influenced by the particle-substrate interface, as in the case of PbS nanoparticle films [6]. Although the equilibrium resistance fluctuation is the dominant noise mechanism in the films having $S_V\tilde{}V^2$, even in this case the slight dependence of S_V/V^2 on film conductance/resistance indicates the presence of a faint nonlinear mechanism. These results support the conjecture that the noise mechanism differs from the one dominating the film conductance and points out to a possible interaction between nanoparticles and the substrate.

Detailed noise measurements performed on the sample NN9, with the lowest noise level, revealed the profound nonequilibrium nature of the noise mechanism, which behaves both sublinearly and superlinearly (Fig. 4). For voltage between (0.055-0.17)V, $S_V\sim V^{0.2}$, while around 0.227V the noise intensity suddenly "commutes" to a higher level. On this level, which develops between about (0.227-0.537)V, the noise intensity is also sublinear: $S_V\sim V^{0..37}$. A strong superliniar behavior, $S_V\sim V^{3.2}$, is observed for voltages larger than 0.537V. Such a $S_V\sim V^3$ dependence is specific to the occurrence of random telegraph signal (RTS) noise. We note also that in the voltage range (0.537-0.778)V, the sample "hesitates" between a linear dependence ($S_V\sim V^2$) and a superlinear one. Also shown in Fig. 4 is the voltage dependence of the frequency exponent (m) whose variation is quite unusual. For instance, the sudden increase of the noise from the first to the second level is accompanied by a transition from 1/f noise, with m slightly smaller than 1, to a diffusion noise ($1/f^{3/2}$). Thereafter, the noise exponent slightly decreases to a value of about 1.34, with some variation around it for higher voltages. No tendency for the exponent to increase to a value of about 2, specific to RTS noise, was observed in the region where $S_V\sim V^{3.2}$.

A V^3 behavior was also reported by Pierre et al. [15] for polystyrene-copper particle composites whose noise power oscillates between two states. Very probable, the strong non-gaussian effects in NN9 are brought about by dynamical current redistribution, as discussed by Seidler et al. [16], a hypothesis arguable by the diffusion noise ($1/f^{3/2}$) observed at the transition between the two noise levels.

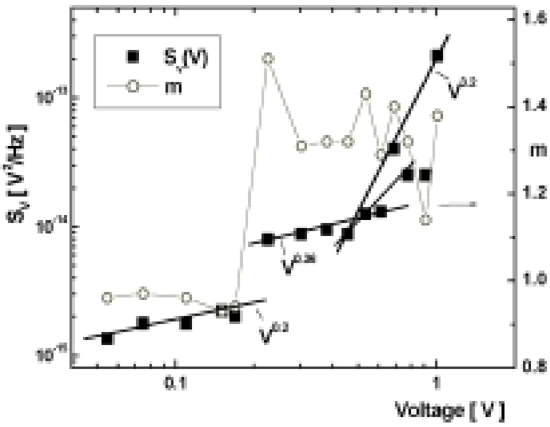

Fig. 4 - S_V and the frequency exponent (m) vs. applied voltage for the sample NN9.

The resistance of this film has been determined as a function of temperature, R(T), in the (8-300)K temperature range. A ratio R(8K)/R(300K)~0.7 was found, suggesting that the conduction would be of metallic type, as in the case reported by Mantese and Webb for some Pt-Al_2O_3 composites [7].

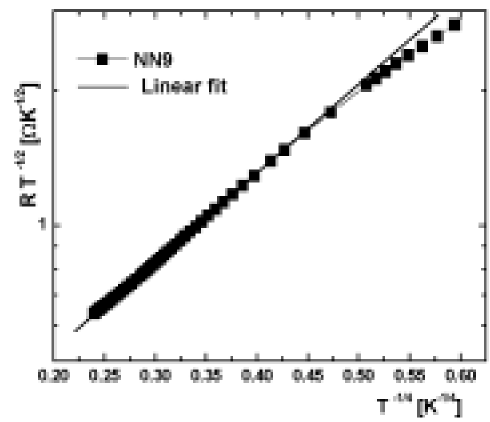

Fig. 5 – Dependence of $RT^{-1/2}$ vs. $T^{-1/4}$ for the sample NN9, in the (8-300)K temperature range.

However, it was not possible to find an activation energy from an Arrhenius representation, $R(T) \sim T^{-1}$, therefore the carriers are not activated to a mobility edge [17] above which extended states exist. In this context, we have fitted R(T) with the Mott's 3D variable range hopping (VRH) equation [17] $R(T)=R_0(T)\exp(T_0/T)^{1/4}$, with a temperature dependent preexponential factor, $R_0(T)$. Considering, as Allen and Adkins [18] for Mott VRH, $R_0(T) \sim T^{1/2}$, $RT^{-1/2}$ vs. $T^{-1/4}$ has been represented as in figure 5. From about 20K to 300K, $RT^{-1/2}$ vs. $T^{-1/4}$ is linear, so that hopping is the conduction mechanism in NN9. Consequently, the variable range hopping is the unique mechanism of both conduction and 1/f noise in this sample. Since the temperature dependence of the preexponential factor in the VRH Mott's law is the signature of phonon-assisted hopping [19], we speculate that hopping-induced 1/f noise could be related to this "hidden" factor.

CONCLUSIONS

Nonequilibrium 1/f noise mechanisms have been identified in some platinum nanoparticle films, in the linear region of the I-V characteristics. In one of these samples, variable range hopping has been found to dominate the conduction and generate 1/f noise. The 1/f noise has been speculatively attributed to the phonons assisting the hopping mechanism.

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