PHYSICAL REVIEW B VOLUME 17, NUMBER 8 15 APRIL 1978

Electrical conduction and current noise in discontinuous platinum films

M. Celasco
Istituto di Fisica Generale dell'Università di Torino, Italy,
Istituto Elettrotecnico Nazionale Galileo Ferraris, Torino, Italy,
and Gruppo Nazionale Struttura della Materia del Consiglio Nazionale delle Ricerche, UR 24, Torino, Italy

A. Masoero and A. Stepanescu
Istituto Elettrotecnico Nazionale Galileo Ferraris, Torino, Italy
and Gruppo Nazionale Struttura della Materia del Consiglio Nazionale delle Ricerche, UR 24, Torino, Italy
(Received 16 November 1977)

Conductivity and current-noise measurements in a wide temperature range on platinum films are reported. The experimental results are interpreted on the basis of a theory developed in a previous paper concerning the conductance mechanisms and the current-noise power spectrum of discontinuous metal films. The much lower current noise shown in these films with respect to the gold ones is interpreted, according to the theory, on the basis of much smaller island structure shown by platinum films. An anomalous behavior of the electrical conductivity and current noise experimentally observed at low temperatures on these films is explained in terms of the adsorption-desorption processes of residual vapor molecules.

I. INTRODUCTION

In a preceding paper[1] a new theoretical model has been worked out to explain the surface conductance versus temperature and the electrical noise mechanism in discontinuous metal films.

The leading idea of this model assumes that in the tunneling process between metal islands within the insulator substrate, the electrons must overcome a potential barrier which is temperature dependent, owing to the shift of the Fermi-level position at the interface metal substrate. This shift is generated by a partial depletion of the surface donor states, located in the insulator surface between metal islands, and it is required in order to ensure electron thermal equilibrium at each temperature.

The current noise is generated as a result of the thermal fluctuation of the potential barrier due to a corresponding fluctuation of the surface charge, due to the ionized donor states.

As shown in Ref. 2 this model rightly accounts for the experimental results obtained on gold discontinuous films deposited on various types of substrates. In particular it explains the nonlinear behavior of the conductivity Arrhenius plots observed in experiments, when a sufficiently wide temperature range is explored, and gives the right order of magnitude for the noise intensity and spectrum. These results cannot in general be obtained by other models based on the thermionic conduction mechanism,[3] direct tunneling,[4-9] or trap-assisted tunneling,[10,11] which explain the temperature dependence of conductivity as an activated process and give a linear Arrhenius plot for the conductivity and a current noise many orders of magnitude lower than observed.

The aim of the present work is to extend the theory of electrical conductivity and current noise[1] previously applied to the gold films[2] to discontinuous platinum films characterized by islands much smaller than the Au ones (see Fig. 1).

Also in this case a strong nonlinear behavior of the conductivity Arrhenius plot is observed, which can be again explained by the theory developed in Ref. 1. Furthermore, a strong reduction of the current-noise intensity with respect to that of gold is also observed, in agreement with what one should expect from the much finer island structure of the Pt films.

Furthermore, owing to the characteristic catalytic properties of platinum, one should expect that at very low temperatures adsorption-desorption processes, magnified by the very fine structure, should originate a dynamical excess noise. Actually, these processes can be evidenced even if an ultrahigh-vacuum system is employed as in our experiments (pressure lower than 10^{-9} mbar).

II. ELECTRICAL CONDUCTIVITY

Discontinuous platinum films having dimensions 4×2 mm and thickness between 50 and 100 Å were obtained by electron beam evaporation of Pt in ultrahigh-vacuum system (10^{-9} mbar) on fused silica. The typical structure of the film is represented in Fig. 1 and is characterized by small islands separated by gaps which are also small especially in critical points where the electrical conduction takes place. Evaporation rate and electrical conductance of the film have been controlled

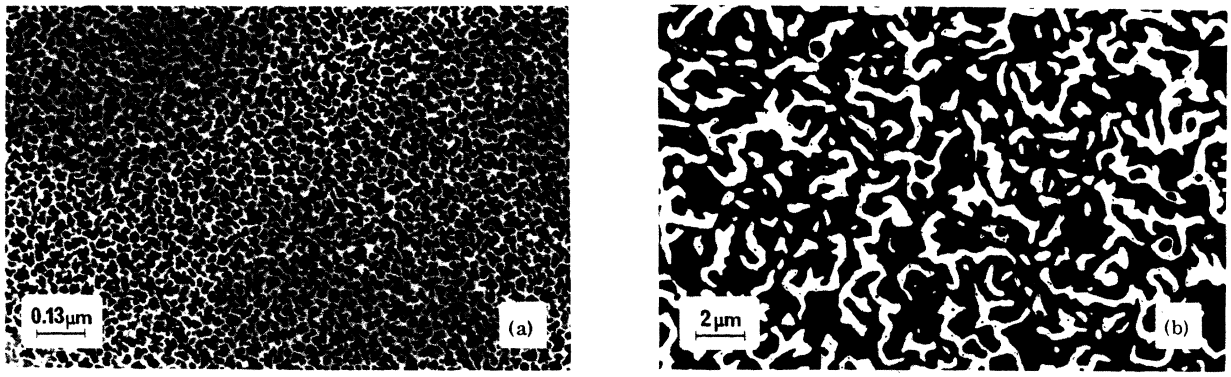

FIG. 1. Electron micrographs of discontinuous films structure evaporated on fused silica substrate: (a) platinum film after annealing at 650 °K in vacuum (10^{-9} mbar); (b) gold film after annealing at 750 °K in vacuum (10^{-9} mbar).

during the deposition on the substrate, which was kept at 650 °K to ensure a good adherence of the metal on the fused silica substrate. All the results were obtained directly on the films within the vacuum system, after annealing at the deposition temperature for 24 h to avoid structural changes on the subsequent measurements.

The experimental results for the surface conductance versus $1/T$ are reported in Fig. 2 and compared with the theoretical ones (continuous line) computed from the tunneling equation obtained in Ref. 1:

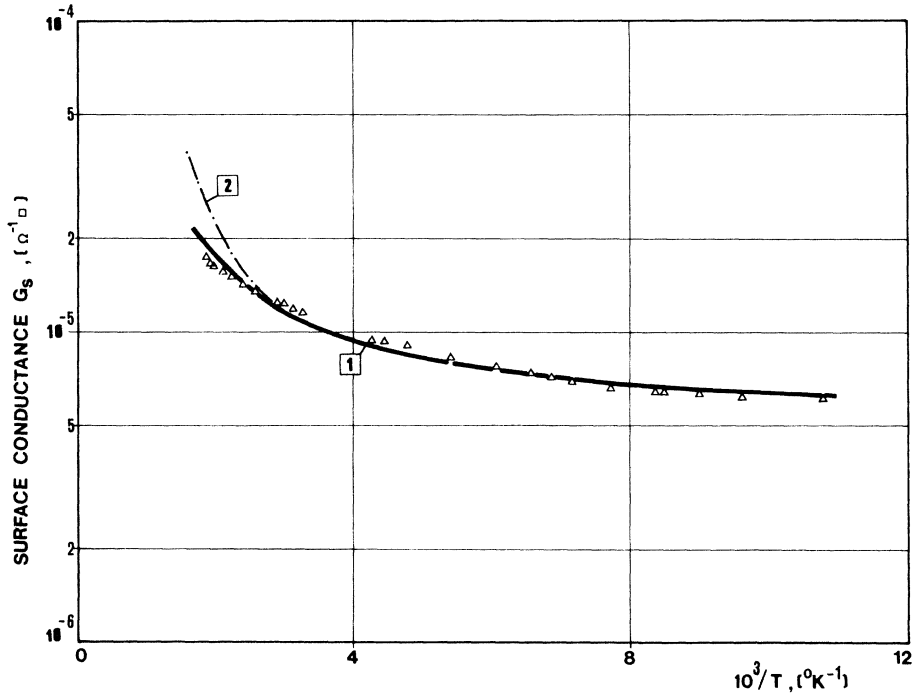

FIG. 2. Logarithmic plot of surface conductance G_s vs the reciprocal absolute temperature for a Pt film evaporated on fused silica substrate. The points are experimental. Continuous curve 1 is theoretical and is computed from the tunneling Eq. (1). When the thermionic contribution is added (dash-dot curve 2), the fitting of the experimental results becomes unrealistic at high temperatures. The best-fit parameters as discussed in the text are $l = 7\times10^{-8}$ m; $d = 1.3\times10^{-9}$ m; $\varphi_B(T)$ is calculated from Eq. (2) with $\chi_m - \chi_3 = 1.15$ eV; $\delta = 5\times10^{18}$ states/m^2; $\varphi_1 = 0.2$ eV; $\epsilon_r^* = \frac{1}{3}\epsilon_r$. As in all the the following figures film dimensions are $L = 2\times10^{-3}$ m; $L' = 4\times10^{-3}$ m.

$$G_1 = l(2m)^{1/2}\left(\frac{e}{h}\right)^2 \varphi_B^{1/2}(T) \times \exp\left(\frac{-4\pi(2m)^{1/2}}{h} d\varphi_B^{1/2}(T)\right). \quad (1)$$

In Eq. (1), m is the electron mass, e is the electron charge, and h is the Plank constant; d and l are the average width and length of the gap between the metal island, respectively; $\varphi_B(T)$ is the temperature-dependent barrier given by the following equation:

$$\varphi_B(T) = \chi_m - \chi_s + \frac{e^2 d}{12\epsilon_0 \epsilon_r^*} \times \left[2d\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} e^{-\varphi_B(T)/kT} - \delta e^{-[\varphi_1 - \varphi_B(T)]/kT}\right], \quad (2)$$

where χ_m and χ_s are the electron work function for the metal and insulator, respectively; ϵ_0 is the vacuum permittivity, and ϵ_r^* is the effective dielectric constant of the substrate; m^* is the effective electron mass at the bottom of the insulator conduction band, k is the Boltzmann constant, and T is the absolute temperature; φ_1 is the energy difference between the bottom of the insulator conduction band and the energy level of the donor states.

In particular, the surface-states density δ is assumed, as in the case of semiconductors surfaces, to be of the order of 10^{14}–10^{15} states per cm^2 and the effective dielectric constant ϵ_r^* of the substrate is assumed to be about 30% of the bulk constant ϵ_r to take into account that the polarization charge screening is localized only on very few monolayers.

The values of φ_1 and d, which are very critical to determine the absolute value and the temperature behavior of the conductivity G_1 have been obtained by fitting the experimental results with Eq. (1). Their values ($\varphi_1 \simeq 0.2$ eV and $d = 13$ Å) turn out to be very reasonable.

With respect to the case of gold films previously treated[2] $\chi_m - \chi_s$ has been given a value of 1.15 eV to take into account the higher work function of platinum. The dependence of G_1 of this quantity is however not critical. Finally, as in the case of gold films it has been assumed $m^* = m$.

The theoretical curve obtained by Eqs. (1) and (2) is reported in Fig. 2 together with the experimental one. The exact values of the parameters involved are reported in the same figure.

The temperature-dependent barrier $\varphi_B(T)$ computed from Eq. (2) has been reported in Fig. 3. It should be noted that the initial drop of the barrier at increasing temperatures is due to a partial depletion of donor states located at the insulator surface, while the increase at highest temperature is attributed to the effect of injected electrons from the metal islands to the conduction band of the insulator.

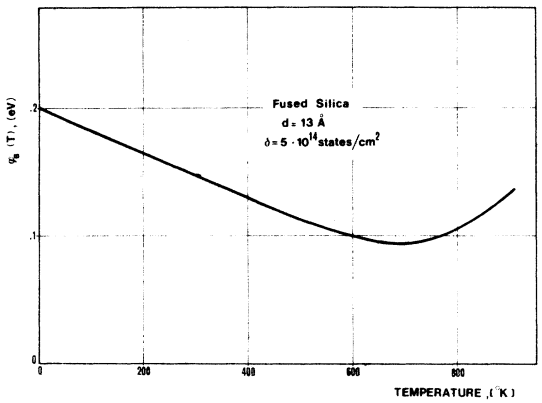

FIG. 3. Potential barrier height $\varphi_B(T)$ vs temperature from Eq. (2) with $\chi_m - \chi_s = 1.15$ eV; $\varphi_1 = 0.2$ eV; $\epsilon_r^* = \frac{1}{3}\epsilon_r$. The value of the relative dielectric constant ϵ_r has been taken as a function of temperature (Ref. 1).

In Fig. 2 (dash-dot line) the thermionic contribution given by

$$G_2 = dl(4\pi m^* e^2 k/h^3) T e^{-\varphi_B(T)/kT} \quad (3)$$

is also shown added to the tunneling term given by Eq. (1). It is seen that a better fit of the experimental results is obtained by neglecting the thermionic component. The reason for this is that Eq. (3) is true if the mean free path of an electron in the insulator conduction band is larger than the gap between metal islands, which probably is not the case near the substrate surface.

III. CURRENT NOISE

Because of the complementary informations given by the current noise on the electrical conduction mechanism of the films,[1,12] noise measurements which refer to the same Pt films have also been reported.

The films were connected to a constant current generator and the voltage noise was detected at the film terminals. The power spectrum of the noise has been measured by 3721A Hewlett-Packard correlator equipped with a 3720A Hewlett-Packard spectrum display.

In the following the relative conductance noise spectrum $\psi_F(\omega)$ of the quantity $\Delta G/\langle G\rangle^2$ is given, referring to a quantity which is independent of the current flowing in the film.

In Fig. 4, $\psi_F(f)$ is reported for three different

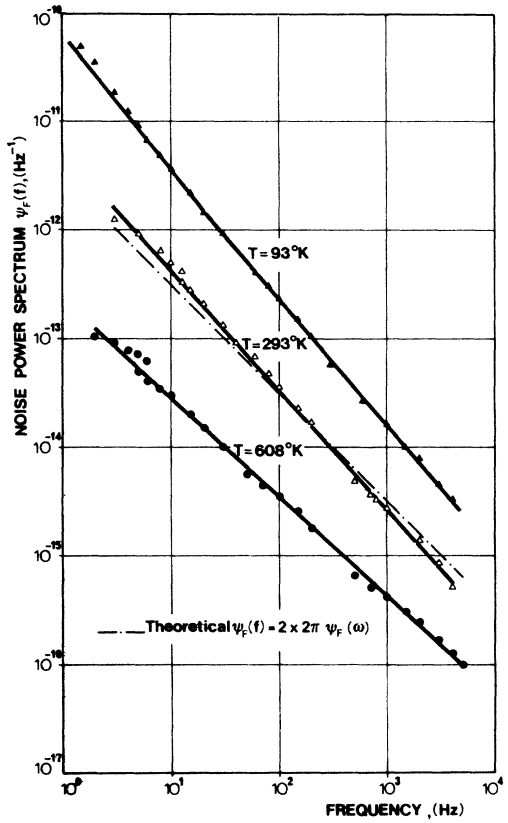

FIG. 4. Power spectra of the relative conductance noise $\psi_F(f)$ at different temperatures in Pt film evaporated onto fused silica substrate. The points are experimental. The theoretical broken line is computed from Eq. (4) with $\ln(\tau'_M/\tau'_m)=16$, $D=1.4\times10^{-7}$ m, and multiplied by $2\times2\pi$ in order to take into account that the experimental spectra refer to the frequency f, and are defined only for $f>0$. The values of the other fit parameters are the same as in the caption of Fig. 3.

temperatures; from the results it follows that the slope of the power spectrum is of $1/f$ type as reported in the literature[12-16] in a rather large range of temperatures, but as in the case of Au films,[2] it becomes consistently more flat (more white) for temperatures above 600 °K. The dash-dot line in the same figure is a theoretical one obtained by the following equation[1]:

$$\psi_F(\omega)=\frac{kTe^2\varphi_B^{-1}(T)}{48\pi\epsilon_0\epsilon_r^* l}\left(\frac{4\pi(2m)^{1/2}d}{h}-\varphi_B^{1/2}(T)\right)^2 \times\frac{1}{\omega}\left(\ln\frac{\tau'_M}{\tau'_m}\right)^{-1} \times[\tan^{-1}(\omega\tau'_M)-\tan^{-1}(\omega\tau'_m)]\frac{D^2L}{L'^3}, \qquad (4)$$

where $\omega=2\pi f$ and all the parameters involved in the fit of the experimental results have been largely discussed in Ref. 1. In particular, the parameters τ'_M and τ'_m, which are the longest and the shortest ionization time, respectively, in the donor ensemble, has been chosen to explain $1/f$ shape of the relative conductance power spectrum, experimentally observed. Both the τ'_M and τ'_m values are not important for the integral noise intensity obtained by integrating Eq. (4). By varying the τ'_M/τ'_m ratio for ten times, one obtained a variation of the equation (4) integral expression less than 20%. D is a parameter which characterizes the average linear dimension along the current direction of the equipotential areas metallically connected, and L, L' are the width and the length of the film, respectively.

In the case of the curve of Fig. 4 calculations have been made for a temperature $T=293$ °K and assuming $\tau'_M=10$ sec, $\tau'_m=10^{-6}$ sec, $D=1400$ Å, $L=2\times10^{-3}$ m, $L'=4\times10^{-3}$ m, while d, l, and $\varphi_B(T)$ are the same as employed in the conductance fitting described above. The integral noise $\langle\Delta G^2\rangle/\langle G\rangle^2$ in a fixed bandwidth (10–10^4 Hz) is reported in Fig. 5. The most important interesting feature is the presence of a maximum near 420 °K. In the same figure is also reported the integral conductance noise on gold film, evaporated

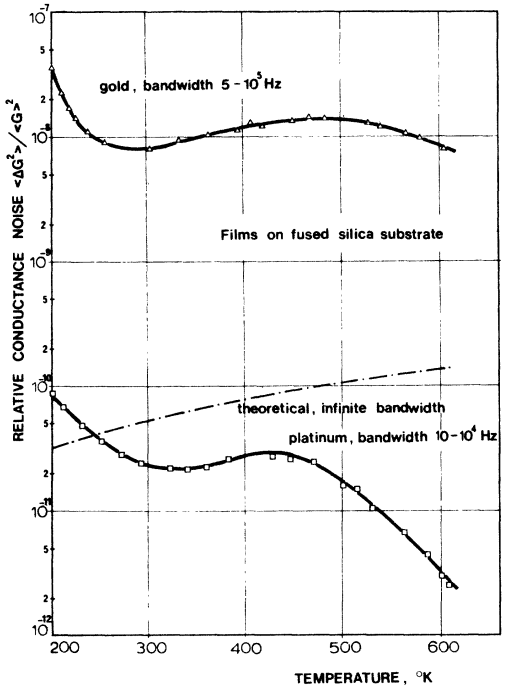

FIG. 5. Relative conductance noise $\langle\Delta G^2\rangle/\langle G\rangle^2$ vs temperature of gold and platinum films with a typical structure as in Fig. 1, evaporated onto fused silica. The points are experimental, the broken fit line for the Pt film is computed from Eq. (5) with $D=1.4\times10^{-7}$ m. For the others fit parameters see caption of Fig. 2.

on the same type of substrate (fused silica) which is two orders of magnitude higher than the platinum conductance noise, as one should expect from the higher D/l ratio value (see Fig. 1). At very low temperatures (100–170 °K) a peaked behavior of the current noise is also observed (see Fig. 6) which can be probably explained in terms of adsorption-desorption processes of vapor molecules.[17,18]

In Fig. 5 the dash-dot line represents the theoretical behavior as given by the equation

$$\frac{\langle \Delta G^2 \rangle}{\langle G \rangle^2} = \frac{1}{48} \frac{e^2 \varphi_B^{-1}(T) kT}{\epsilon_0 \epsilon_r^* l} \times \left(\frac{4\pi}{h} (2m)^{1/2} d - \varphi_B^{-1/2}(T) \right)^2 \frac{D^2 L}{L'^3} . \quad (5)$$

It is seen that the order of magnitude of the theoretical noise intensity is in a good agreement with the experimental results taking into account that the last ones refer to a reduced bandwidth, while Eq. (5) is relative to a virtually infinite bandwidth.

IV. LOW-TEMPERATURE ANOMALIES IN RESISTIVITY AND CURRENT NOISE

A large anomaly in the noise and resistivity has also been observed in Pt films having the structure shown in Fig. 1(a), at rather low temperatures. The experiments were made at a pressure below 10^{-9} mbar by detecting the current noise, film resistance, and the vacuum system pressure, during the temperature increase after cooling the film to liquid-nitrogen temperature, as reported in Fig. 6. A large increase of the pressure from 10^{-9} up to 10^{-6} mbar has been detected at temperature near −130 °C. This fact, which is probably due to a physical desorption of the adsorbed water molecules from the substrate, is responsible for the large anomalies, which are present in the conductivity of the films and for the current noise peaks shown in the figure (the corresponding increase of the relative conductance noise is larger than two orders of magnitude).

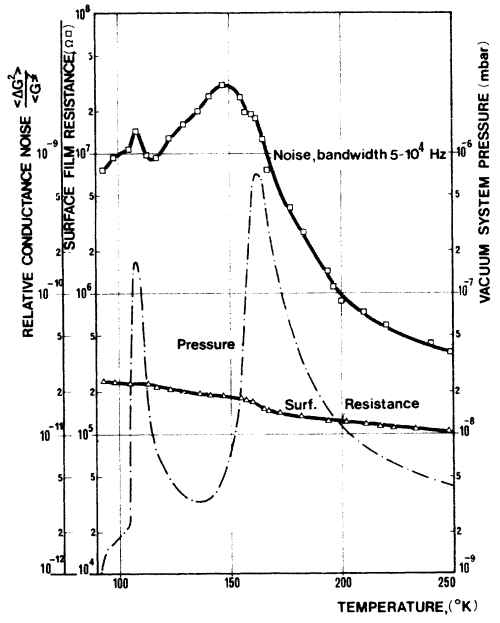

FIG. 6. Experimental behavior of the excess integral noise, the surface resistance, and the vacuum system pressure during the heating of a Pt film from near liquid-nitrogen temperature to room temperature as a consequence of the desorption processes on the film surface.

It can be pointed out that the adsorption processes of H_2O on substrates at very low temperatures from the residual gases present in the vacuum system is not a new fact till now; with the secondary-ions-mass-spectrometry analysis of metal and insulator substrate, the presence of ionic compounds of the type $H^+(H_2O)_n$ (with $1 < n < 11$) having the activation energy near the sublimation heat of ice[19] has been detected in the temperature range between −130 and −120 °C.

Similar adsorption-desorption surface processes have also been observed on continuous semiconducting films. In particular, very thin nonstoichiometric films of the type W_2O_{5-x} show an excess noise if exposed to a low partial pressure (10^{-5} mbar) of water[17] and other several organic compounds.[18] On the basis of the proposed model a qualitative explanation of the noise behavior at low temperatures in the Pt films will be given in Sec. V.

For what concerns the resistance, its anomalies shown by the film in correspondence of the pressure desorption peaks are probably due to a simple cooling effect on the film related to the desorption process. Owing to the negative temperature coefficient of the resistivity a cooling on the film is associated with a resistance increase, as experimentally observed.

V. DISCUSSION

As it was suggested in Sec. I, following the proposed theory,[1] the conduction processes involve three main mechanisms, i.e., (a) direct tunneling of electrons between metal islands through the substrate, (b) tunneling of electrons from surface states of the insulator to the metal islands, and (c) thermal injection of electrons from the metal to the conduction band of the insulator, which is responsible for the drop of the noise intensity at the highest temperatures. The last contribution is present at the highest temperature only.

According to the experimental results the therm-

ionic contribution seems to be negligible. This fact can be explained by taking into account that the electron mean free path in the insulator near the surface is shorter than the island gaps.

The main assumption of this model concerns the existence of donorlike levels located at the surface states of the insulator, the surface states forming a single highly degenerate level below the conduction band. In the comparison of the theoretical curves obtained by Eq. (1), a reduced coefficient $\beta = \frac{1}{3}$ has been employed for the dielectric constant ϵ_r because we can assume that the active trapped charge is only a few atomic spacings apart from the metal island. The difference between the metal and insulator work functions $\chi_m - \chi_s$ has been taken equal to 1.15 eV in agreement with data in the literature,[11] while the best-fit parameter φ_1 was chosen equal to 0.2 eV, value found in gold films evaporated on fused silica and sapphire substrates.

Finally, the average width of the tunneling barrier d was chosen in each case to yield the correct value of the conductivity, while the best fit of the integral noise has been obtained by assuming $D/l = 2$ as suggested by the micrographs shown in Fig. 1.

The fit obtained between the experiments and theoretical results shows that the model, which assumes that the noise is generated by the modulation of the potential barrier between metal islands induced by statistical fluctuations, gives not only the $1/f$ behavior of the power spectrum as in previous theories[13,14] but also the right order of magnitude on the noise.

It can be noted that the noise intensity experimentally observed on platinum films is smaller than that observed on gold ones. This fact is well accounted for by the theory,[1] which implies a strong dependence of the noise on the structural parameters of the film, like D and l [see Eqs. (4) and (5)].

As in the case of gold films the power spectrum tends to become consistently more white at high temperatures. This effect has been explained in Ref. 1 as due to the thermal-injection effect of electrons from the metal to the conduction band of the insulator.

For what concerns the low-temperature behavior, the experimental noise intensity is rather higher than the theoretical one, an effect which has also been observed in the Au films.[2] In the particular case of Pt, since the adsorption-desorption phenomena occurring at low temperature are enhanced by the fine-grained structure of the films, the experimental noise intensity is almost three orders of magnitude higher than the theoretical one, while the electrical resistance shows a sharp anomaly.

On the basis of the proposed model, one could try to explain the observed low-temperature behavior of noise and conductivity in terms of variation of the barrier height. Actually the adsorption-desorption processes described in Sec. IV allow a local variation of surface-donor-states density, which is strictly related to barrier height $\varphi_B(T)$ [see Eq. (1)]. However, for the noise intensity, an explanation of the large increase observed (almost three orders of magnitude) in terms of a lowering of the barrier height is not possible, if one does not use an unrealistically small value of the barrier height.

The only assumption which can justify the noise behavior at low temperatures seems to be related to the macroscopic dynamical processes of vapor-molecule evaporation-condensation on the film surface, present in the vacuum system even at pressures below 10^{-8} mbar. The excess noise source may be generated by the fluctuation of the vapor molecules adsorbed on the surface of the film, which modulates the potential-barrier height between metal islands.

VI. CONCLUSIONS

The experimental results for the conductivity and current noise on platinum films are interpreted on the basis of the previous theory.[1] In particular the predicted electrical-conduction behavior versus temperature has an experimental confirmation over a very large temperature range. As in the case of the gold films the contribution due to the thermionic current must be disregarded to fit the experimental results which can be explained by the electron mean free path being much smaller in the substrate than in the vacuum.

The noise intensity observed on Pt films evaporated on a fused-silica substrate is two to three orders of magnitude lower than observed on gold films deposited on the same substrate (see Fig. 5). This fact is well accounted for by the theory owing to a dependence of the current-noise intensity on the structural parameters D and l of the film [see Eq. (5)]. Actually the very fine structure of the Pt islands gives a value of D^2/l about two to three orders of magnitude lower than with gold films.

However, the conductivity and noise behavior versus temperature is very similar to that of Au films, as one could expect since the behavior of these quantities is more dependent on the discontinuous structure of the film than on the type of metal.

Also in the case of a platinum film, a maximum in the noise intensity is experimentally observed near 450 °K (see Fig. 5), which may be interpreted

by assuming that above this temperature a direct injection of electrons into the conduction band of the insulator takes place.

Also due to the same effect is the decrease in the noise slope (from $1/f$ to $1/f^{\alpha}$, with $\alpha < 1$) at temperature higher than 450 °K, as in the case of Au films.

Finally, anomalies of the current-noise intensity and electrical resistance have been observed at low temperatures. These effects can be explained by considering that adsorption-desorption processes, which are responsible for a dynamical excess noise, can occur in the film substrate.

ACKNOWLEDGMENTS

The authors wish to thank Professor Piero Mazzetti and Professor Giorgio Montalenti for useful discussions.

[1]M. Celasco, A. Masoero, P. Mazzetti, and A. Stepanescu, Phys. Rev. B 17, 2553 (1978).
[2]M.Celasco, A. Masoero, P. Mazzetti, and A. Stepanescu, Phys. Rev. B 17, 2564 (1978).
[3]K. Van Steensel, Philips Res. Rept. 22, 246 (1967).
[4]C. A. Neugebauer and M. B. Webb, J. Appl. Phys. 33, 74 (1962).
[5]T. E. Hartman, J. Appl. Phys. 34, 943 (1963).
[6]J. G. Simmons, J. Appl. Phys. 35, 2655 (1964).
[7]R. Kieznan and D. W. Stops, J. Vac. Sci. Technol. 9, 433 (1971).
[8]D. S. Herman and T. N. Rhodin, J. Appl. Phys. 37, 1594 (1966).
[9]A. Barr and R. D. Finney, Thin Solid Films 24, S11 (1974).
[10]A. A. Milgram and C. Lu, J. Appl. Phys. 37, 4773 (1966).
[11]R. M. Hill, Proc. R. Soc. Lond. A 309, 377 (1969).
[12]J. L. Williams and I. L. Stone, J. Phys. C 5, 2105 (1972).
[13]J. L. Williams and R. K. Burdett, J. Phys. C 2, 298 (1969).
[14]L. S. Kremenchugsky, A. F. Malnyev, and V. B. Samoilov, Ukr. Fiz. Zur. 8, 762 (1963).
[15]J. P. Borel, J. Phys. Rad. 17, 224 (1956).
[16]A. Blanc-Lapierre and N. Nifontoff, J. Phys. Rad. 17, 230 (1956).
[17]A. Masoero, P. Mazzetti and A. Stepanescu, Vacuum 27-4, 349 (1977).
[18]A. Masoero, P. Mazzetti and A. Stepanescu, Comptes-Rendus du Troisieme Colloque International de Physique et Chimie des Surfaces Solides, Grenoble, 1977 (unpublished).
[19]M. De Paz and C. Macciò, Z. Naturforsch. A 30, 831 (1975).

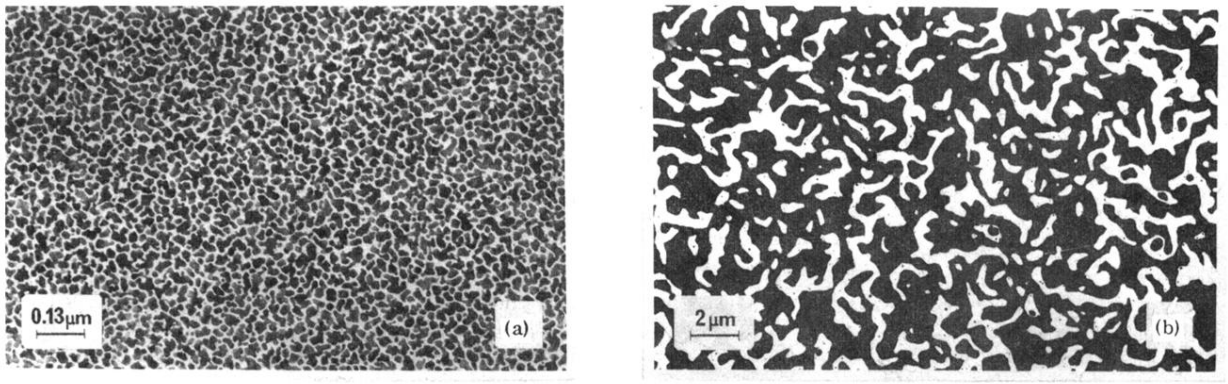

FIG. 1. Electron micrographs of discontinuous films structure evaporated on fused silica substrate: (a) platinum film after annealing at 650 °K in vacuum (10^{-9} mbar); (b) gold film after annealing at 750 °K in vacuum (10^{-9} mbar).