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Photoemission from very thin films of strontium. Action of an electric field

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Properties of photoemission from very thin films of strontium have been studied on the one hand in terms of the films' structure, and on the other hand when the films were submitted to the action of an external electric field applied perpendicularly to the metallic surface. The thin films were prepared by thermal evaporation and condensation on a quartz substrate in an ultrahigh vacuum (5×10^{-10} Torr). Mass thicknesses were between 0.5 and 33 nm. The electric field could reach 985×10^{3} V m^{-1}. The work function varies with mass thickness of the thinnest films and exhibits two minimums for thicknesses $d_1 = 2.5$ nm and $d_0 = 7.5$ nm. It is constant, and equal to 2.64 eV, for all films thicker than 12 nm. A strong external electric field $\vec{E}$, of correct orientation, applied perpendicularly to the surface of the film brings on a decrease $\Delta\Phi_E$ of the work function. $\Delta\Phi_E$ varies linearly as a function of $\sqrt{E}$ and also depends on the thickness of the films; it is minimal for thicknesses d_1 and d_0. This set of results can be deduced from the variation of the electronic double layer on the surface.

I. INTRODUCTION

A certain number of fundamental parameters relating to the electronic structure of the solid can be determined by studying metals in the form of thin films. The energy distributions of the bulk bands or the density of the surface charges can thus be obtained. Investigation of the optical properties of thin films provides information concerning the existence and energies of plasmons.[1] Information can also be deduced as to the structure of the energy bands. This has been done, for example, by Donovan, Spicer, Bennett, and Ashley.[2] Study of photoemission provides a new contribution which completes the above results. Let us quote, in particular, the works of Eastman[3] on photoemission of thin metallic films, as well as those of Bush, Campagna, and Siegmann[4] on electron spin polarization.

We have studied the photoemission of thin films of strontium in terms of variation of structure and in terms of the action of an external electric field of correct orientation, perpendicular to the surface of the films. The structure of the latter is conveniently elicited by the mass thickness d. It is known that, when d is very small, the film is composed of small discrete islands. When d grows, the size and number of islands increases. The film then becomes lacunar and finally continuous. Endriz and Spicer[5] have shown the influence of surface roughness on the photoemission properties of aluminum films. Let us remark that, when mass thickness increases, for example from 1 to 30 nm, the extent of the surface of the metal in relation to that of its bulk is modified, and the quantities which depend on the surface vary in a different way from those connected to the bulk. This should provide a means of distinguishing the former from the latter.

The potential barrier at the metal-vacuum interface depends on the density of superficial charges. Consequently it is a physical quantity associated to the surface. It is therefore interesting to study thin metallic films by means of photoemission with energies close to the photoelectric threshold. In this range, there is great surface influence and the potential barrier is equal to the work function Φ. This latter is calculated from quantum yields ρ normalized to the absorbed flux using Fowler's equations.[6] Although these equations were originally calculated from a simple theoretical model they can nevertheless be employed. Meessen[7] has shown that they remain correct with better models.

The second part of this study concerns the effect of a constant electric field $\vec{E}$, perpendicular to the surface of the film, on the work function Φ. This study is complementary to the preceding one, as an electric field $\vec{E}$ essentially acts on the surface of the solid and modifies the density of charges there. The interest of these experiments has been shown by Lundqvist, Mountfield, and Wilkins.[8] We have studied the action of electric fields within a range of some V m^{-1} to 10^{6} V m^{-1}. These values are lower than those which involve field emission. With higher values of $\vec{E}$ there would be a risk of greatly modifying the structure of the film, and it would then have been difficult to compare the effects of structure with those of the electric field.

Ultrathin films of alkaline earth metals exhibit special properties[9] and results already obtained from studying photoemission of calcium have prompted us to undertake a study of strontium.

II. EXPERIMENTAL CONSIDERATIONS

A. Experimental conditions

The thin film of strontium, which constitutes the photocathode, is prepared by thermal evaporation and condensation on a plane quartz substrate in ultrahigh vacuum ($\sim 5\times10^{-10}$ Torr). The apparatus is the same as that used to study calcium.[10,11] The radiation source is a xenon lamp emitting a continuous spectrum. The radiation's direction of propagation is perpendicular to the surface of the film.

All the films are prepared identically, retaining, in particular, the same evaporation geometry and the same deposition rate (mass of metal deposited per surface unit and time). The latter is approximately 0.1 nm/sec. Recent studies[12,13] show the influence of evaporation conditions on the structure of thin films. As a preliminary the metal is carefully degassed several times. Indeed, in the case of barium, Bondarenko and Makhov[14] show that insufficient preliminary degassing brings about a great change in the film and the work-function values are then incorrect. After deposition, the study of the film is made without interruption of the ultrahigh vacuum. The mass thicknesses are monitored with a quartz crystal oscillator. They fall within a range of 0.5–33 nm approximately. Reale has shown[15] that the films of alkaline earth metals obtained under these conditions are polycrystalline.

Once the film has been deposited it must stabilize before a study can be undertaken. Indeed, during the few minutes following deposition, the structure of a thin film evolves by coalescence[16] and electrical resistance measurements, for example, reveal great changes.[17] The film, on its quartz substrate, is placed in front of a plane metallic anode. The electric field, applied perpendicularly to the surface of the film, depends on the potential V of the anode, the film constituting the photocathode which is maintained at zero potential. When the potential applied to the anode, still positive, increases, the photoemission intensity reaches saturation at approximately 20 V (Fig. 1), whatever the incident radiation. The saturation level is displayed up to 200 V.

It should be remarked, as will be seen subsequently, that with much higher potentials (up to 10 000 V) the current I goes on increasing slightly. During photoemission measurements the potential applied to the anode is always higher than 20 V. It is therefore the saturation currents which are measured, so that Fowler's theory[6] can be used.

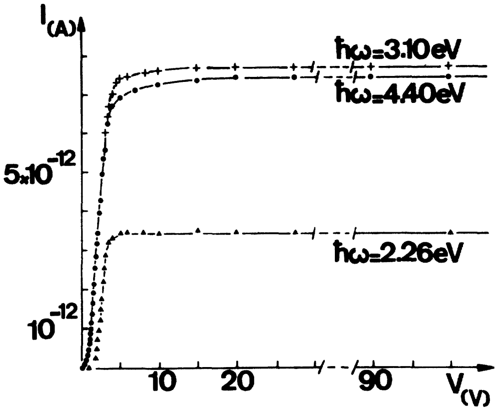

FIG. 1. Intensity I as a function of potential V for incident radiations of different photon energies.

B. Variations of quantum yield as a function of a pressure rise in the ultrahigh compartment

Alkaline earth metals are particularly liable to deterioration. Helms and Spicer[18] have obtained, by ultraviolet photoelectron spectroscopy, an increase of photoelectric yield versus oxygen exposure. Thus the extent of yield variations when pressure passes from 5×10^{-10} Torr to atmospheric pressure is determined first. Figure 2 represents these variations for three films of strontium of different mass thicknesses. The shape of the curves is the same, but the yields are modified starting from 8×10^{-8} Torr. This modification remains small up to 10^{-7} Torr. Between 5×10^{-6} and 10^{-5} Torr, according to the thickness of the

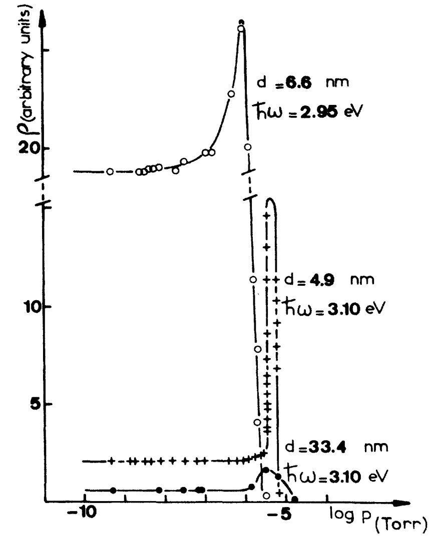

FIG. 2. Variations of quantum yield as a function of the base-10 logarithm of pressure for three strontium films of different mass thicknesses.

films, the yield increases and then decreases rapidly. When mass thickness is less this peak is all the greater. The decrease down to zero, and the irreversibility of this phenomenon, seem to indicate that it consists of a complete modification of the film, not only at the surface but also in bulk.

C. Investigation, in ultrahigh vacuum, of the variations of the work function as a function of time

Figure 3 gives the variations of the work function as a function of time when the film is maintained under a pressure of approximately 5×10^{-10} Torr. This work function is determined from the yields using Fowler's graph method.[6] The origin of the time corresponds to the end of the evaporation. As previously, it was remarked that the films of small mass thickness are the first to be modified. The work function of a film 18 nm thick remains constant for 10 h, whereas for a film of 1.5 nm this time is reduced to 4 h. After this level there is a decrease followed by an increase. The minimum occurs approximately 20 h after deposition with a thick film, and 10 h later with a film of 1 nm. This minimum corresponds to a maximum yield. These variations are analogous to those observed with a rise in pressure. In both types of experiments the yield variations occur in the same direction.

To avoid these effects, the duration of photoemission measurements was always less than 4 h and systematic checks were carried out at the end of measurement.

III. VARIATIONS AS A FUNCTION OF MASS THICKNESS

A. Quantum yields

The directly measurable physical term by which the work function can be monitored is the quantum yield ρ normalized to the flux absorbed. This yield depends on the macroscopic structure of the film, that is to say on its mass thickness, and on the photon energy $\hbar\omega$ of the incident monochromatic radiation. Figure 4 shows the yield variations, as a function of thickness d of the films, for two monochromatic radiations situated in the near ultraviolet. There are two peaks which occur, respectively, for thicknesses $d_1 = 2.5$ nm and $d_0 = 7.5$ nm.

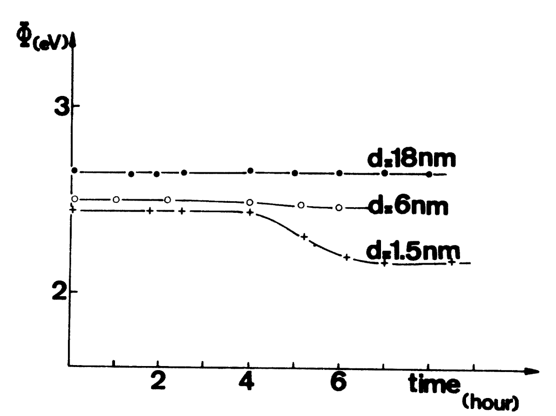

FIG. 3. Variations of work function as a function of time for three strontium films of different thicknesses.

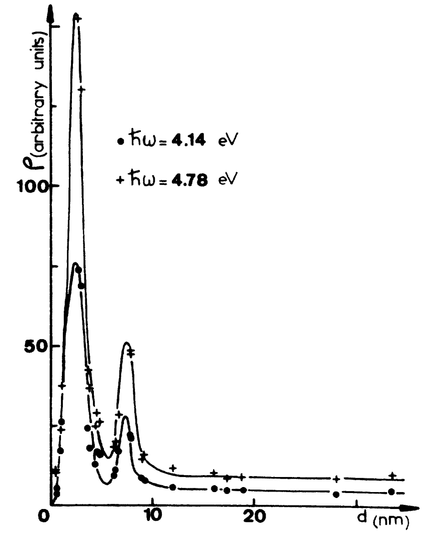

FIG. 4. Variations of strontium quantum yield as a function of thickness for two monochromatic incident radiations.

These curves are analogous to those obtained

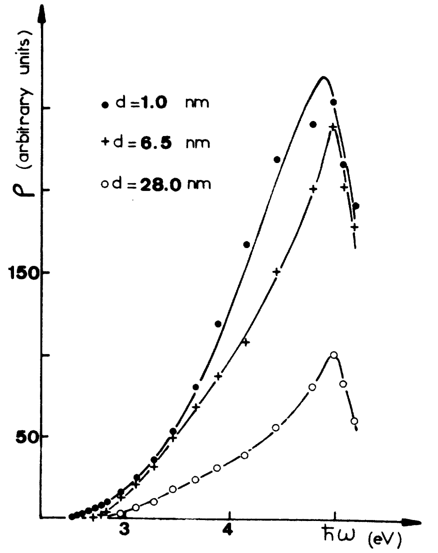

FIG. 5. Variations of quantum yield as a function of the energy $\hbar\omega$ of the incident radiation for three films of strontium of different thicknesses.

for calcium.[10] However, with this latter metal, the maximum corresponding to $d = 2.5$ nm is lower than that obtained for $d = 5.5$ nm. For strontium films thicker than 12 nm the yields no longer depend on thickness, within experimental error. Studies effected with metals such as aluminum, gold, and silver, deposited in thin films on an insulated substrate, generally only display a single maximum.[19]

The values of energies $\hbar\omega$ of incident radiations are within a range of 2 to 5.3 eV. The quantum yields exhibit a peak for approximately 5 eV, whatever the thickness considered (Fig. 5).

The study of quantum yield is important, as it gives a direct experimental account without the intervention of any theory. However, if we wish to obtain a characteristic physical quantity of the solid the work function must then be determined.

B. Work functions

With each film of strontium the work function Φ can be determined by means of the spectral sensibility curve superposed on Fowler's theoretical curve F. In general, with all films thicker than 2.5 nm, the superposition of experimental dots on the theoretical curve F is effected over a wide range (Fig. 6: $\hbar\omega/kT$ between 100 and 155). With $\hbar\omega/kT$ values greater than 155, the experimental dots are situated below the values calculated.

On the other hand, with all films thinner than 2.5 nm, the experimental dots fit correctly onto Fowler's curve only in the neighborhood of the threshold (Fig. 7: $\hbar\omega/kT$ ranging between 90 and 110). With greater photon energies, the yields measured are higher than those calculated (Fig. 7: $\hbar\omega/kT$ ranging between 110 and 200).

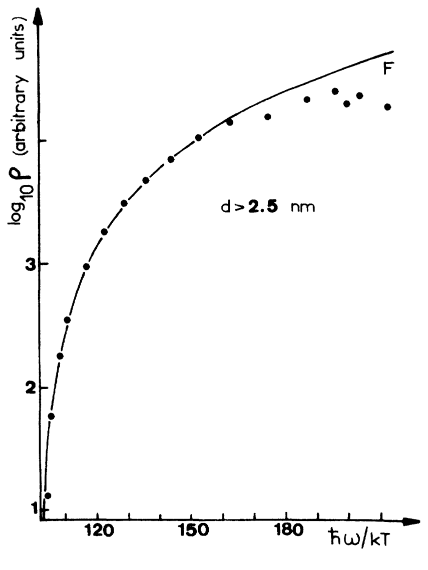

FIG. 6. Variations of the base-10 logarithm of yield as a function of $\hbar\omega/kT$ for a film thicker than 2.5 nm. The dots are experimental and F is Fowler's theoretical curve.

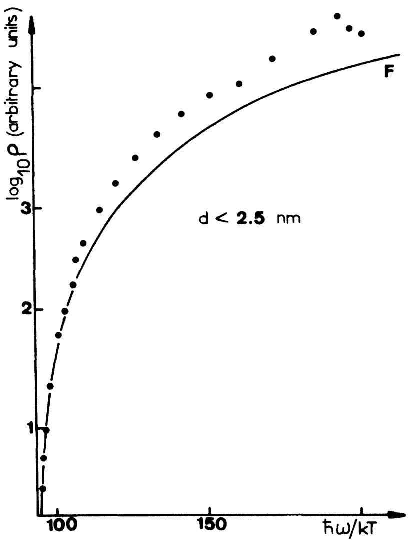

FIG. 7. Variations of the base-10 logarithm of yield as a function of $\hbar\omega/kT$ for a film thinner than 2.5 nm. The dots are experimental and F is Fowler's theoretical curve.

In each case, a work function Φ can be determined for each film. Its variations, as a function of mass thickness d, are shown in Fig. 8. The work function exhibits two minimums for thicknesses $d_1 = 2.5$ nm and $d_0 = 7.5$ nm. A minimum of Φ therefore corresponds to each peak yield. For films thicker than 12 nm the work function is constant and equal to $\Phi_m = 2.64$ eV. Analogous variations, which however only exhibit a single minimum, have been observed with metallic thin films using both photoemission[19] and other methods.[14]

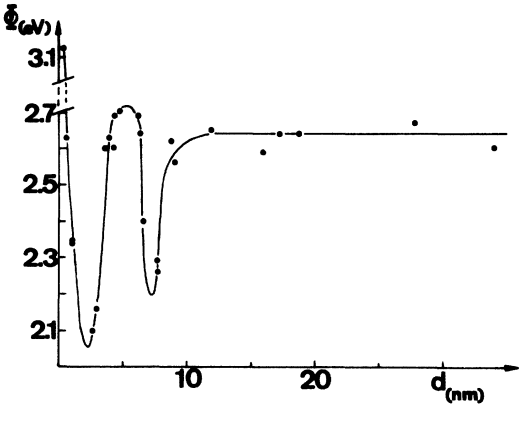

FIG. 8. Variations of work function Φ as a function of the mass thickness d of strontium films.

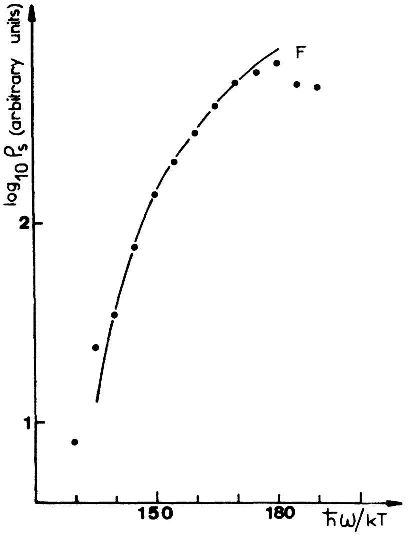

FIG. 9. Variations of the base-10 logarithm of yield ρ_s corresponding to a second photoelectric threshold. The dots are deduced from experiment. The curve F is traced from Fowler's equations. The film is 1 nm thick.

This also applies to the studies of Melmed, Carrol, and Meclewski[20] on the field emission of aluminum films deposited on tungsten.

Figure 7 shows that, with films thinner than $d_1 = 2.5$ nm, the yield obtained experimentally is higher than that foreseen by Fowler's theory for energies $\hbar\omega$ far from the photoelectric threshold $(\hbar\omega/kT > 110)$. An explanation of this abnormal increase may be stated as follows: the experimental yield ρ_{ex} is equal to the theoretical yield ρ_{th} increased by a quantity ρ_S which has the same dimension as a yield: $\rho_{ex} = \rho_{th} + \rho_S$.

A new work function Φ_S can be determined using the curves $\log_{10}\rho_S = f(\hbar\omega/kT)$, compared with Fowler's theoretical curve (Fig. 9). This latter therefore corresponds to a second photoelectric threshold. The value obtained, $\Phi_S = 3.3$ eV, is the same for all thicknesses less than 2.5 nm. Φ_S does not exist for higher values of d.

IV. EFFECT OF AN ELECTRIC FIELD

A. Quantum yields

The geometry of the photocathode-anode set is such that to each potential V applied to the anode there corresponds an electric field $\vec{E}$ perpendicular to the surface of the film. In the preceding study, the positive potential V_0 chosen is such that the field $\vec{E}_0$ is weak enough to trap all the photoelectrons emitted, its action on the potential barrier is negligible.

We shall examine the results obtained when $\vec{E}$ has high values, which may reach 985×10^3 V m^{-1}, corresponding to a potential V of 10^4 V. The saturation observed in the curves $I = f(V)$ for low values of V (Fig. 1) is then seen to be merely apparent. For high-field values the yield increases (Fig. 10). The magnitude of this increase depends on the energy $\hbar\omega$ of the incident radiation and the structure of the film.

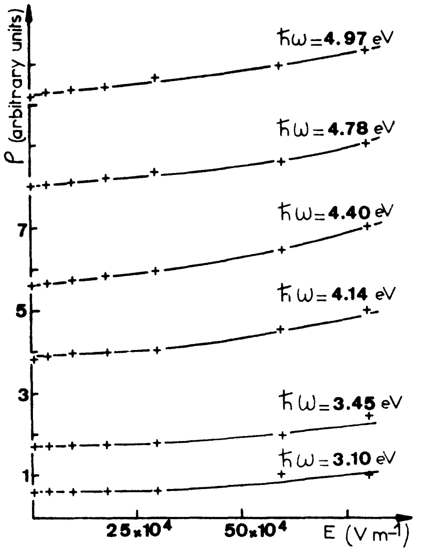

FIG. 10. Quantum yields ρ are plotted against the electric field for different incident radiations of energy $\hbar\omega$. The film is 28 nm thick.

The graphs of the relation $\rho = f(\hbar\omega)$, for a given film, all have the same shape, whatever the value of $\vec{E}$. They exhibit a peak towards 5 eV (Fig. 11). When the field increases the photoelectric thresh-

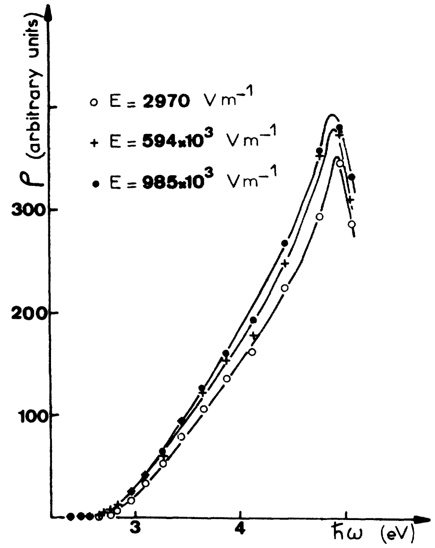

FIG. 11. Variations of quantum yield ρ as a function of the energy $\hbar\omega$ of incident radiation for three values of the electric field. The strontium film is 4.5 nm thick.

old shifts towards low energies and the spectral sensibility curves are modified, which implies a relationship between the work function and the electric field.

B. Work function

As the yield increases with the electric field, a decrease of work function should be expected. This is indeed what occurs. Let Φ_E be the work function when a field $\vec{E}$ is applied to the surface of the film and Φ_0 the work function when this field is negligible. The difference: $\Delta\Phi_E = \Phi_E - \Phi_0$ is negative for all the films. With a massive metal of perfectly plane surface Schottky's[21] theory gives a linear decrease $\Delta\Phi_E$ as a function of $\sqrt{E}$. The variations of $\Delta\Phi_E = f(\sqrt{E})$ for several films of strontium are shown in Fig. 12. They are straight lines and the slope, which is always negative, changes with thickness. With very thin films the absolute value of the slope is low and with thick films it reaches a constant value. In this figure, the straight line S is traced from Schottky's relation.[21] Normally it should correspond to the thick films with films having a surface close to Schottky's model. Quantitatively, the agreement between the experimental values and the values calculated is not very good.

For a given electric field, the variations of the decrease $\Delta\Phi_E$ as a function of mass thickness d are given in Fig. 13. $\Delta\Phi_E$ goes through two minimums, of abscissae situated, respectively, between 1 and 3 nm and between 6 and 8 nm. These values correspond to the thicknesses d_1 and d_0 already mentioned in Sec. IV B. Above 20 nm, the decrease $\Delta\Phi_E$ is constant and equal to $\Delta\Phi_m = -0.01$ eV for a field of 297×10^3 V m^{-1}. In such a representation, Schottky's relation[21] takes the form of a straight line S parallel to the abscissa (Fig. 13). Thus there are great differences between experimental and calculated results.

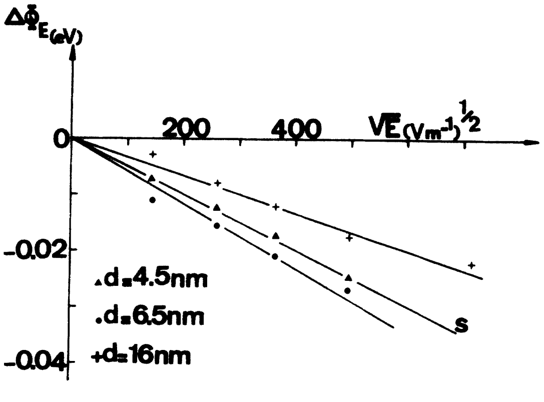

FIG. 12. Variations of the decrease $\Delta\Phi_E$ of the work function as a function of the square root of the electric field. The straight line S is deduced from Schottky's relation.

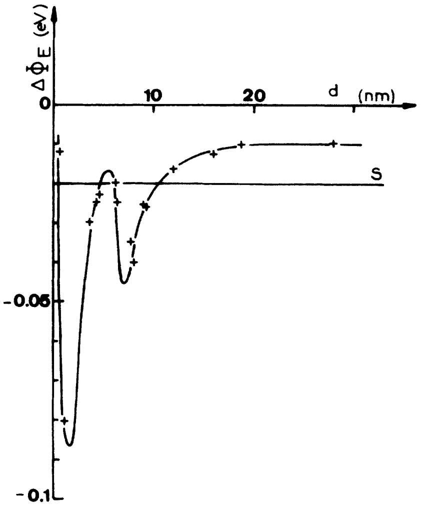

FIG. 13. Variations of the difference $\Delta\Phi_E$ between the work function Φ_E corresponding to presence of an electric field $E = 297\times10^3$ V m^{-1} at the surface of the film and the work function Φ_0 for a negligible electric field. The dots are deduced from experiment. The straight line S is determined from Schottky's relation.

V. DISCUSSION

A. Remarks on the structure of the films

Mass thickness is a useful parameter by means of which the structure of the thin film can be elicited. With metals, this structure is rather well known due to the fact that numerous electron microscopy studies have been carried out during the last few years. Let us cite, in particular, those of Kazmerski and Racine[13] on gold and those of Rasigni, Palmari, and Rasigni[22] on magnesium. Blanc[9] has made a study of alkaline earth metals under experimental conditions analogous to ours. When the thickness is very small, less than 1 nm, the metallic deposit is composed of very small discrete islands. When the thickness increases the size and number of islands also increase. Subsequently the films become lacunar, that is to say composed of veritable metallic corridors on the insulator substrate; with alkaline earth metals, thicknesses are then approximately 10 nm. Finally, with greater thicknesses, the films are almost continuous and the vacancies are negligible. It should however be pointed out that if the conditions of preparation vary (vacuum, deposition rate, substrate, etc.), a same mass thickness can correspond to two different structures; but the sequence—films which are granular, lacunar, and then continuous—remains: it is the critical thicknesses which are shifted. In particular, Blanc and Rivoira[23] have shown that for all thicknesses less than 7 nm the films are granular and exhibit a characteristic optical absorption. This takes the form of a maximum of quantity $2\nu\kappa d/\lambda$ for an incident energy $\hbar\omega$ of approximately 1 eV. This absorption disappears with thicknesses greater than 8 nm, that is to say for lacunar films. The critical thickness is situated between 7 and 8 nm and corresponds to the change of a granular structure into a lacunar structure. Three domains can therefore be taken into consideration:

$d < 7.5$ nm granular films,

$7.5 < d < 12$ nm lacunar films,

$d > 12$ nm quasicontinuous films; the vacancies no longer influence the photoemission.

It should be remarked that the critical thickness d_0 is determined not only by studying the optical properties but also by investigating the photoemissive ones.

The results to be interpreted are essentially: the shape of the curves $\Phi = f(d)$, the variations of the decrease $\Delta\Phi_E = f(d)$, and the analogy between the variations of Φ and those of $\Delta\Phi_E$.

An interpretation according to plasma resonance does not appear to be suitable, as the energies involved in the experiments reported here are too low.[24] The similarity between the forms of the curves of Φ and $\Delta\Phi_E$ suggests that the effect of structure and of the electric field is to perturb the same characteristic parameter of the solid. Now, an external electric field acts on the charges situated in the near neighborhood of the surface. Among the different components of the work function one must therefore look for those which call for the presence of a metal-vacuum interface.

B. Work functions and structure of the films

The variations of the work function Φ as a function of thickness exhibit two minimums. The first, of abscissa $d_1 = 2.5$ nm, corresponds to a granular structure. It is probably connected with the appearance of conduction. The conduction mechanism of ultrathin films has been studied by Boiko, Palatnik, and Synelnikov.[25] Dittmer[26] has suggested the presence of an assisted tunnel effect. In our experiments we observed analogous phenomena from the photoemission angle. Existence of a second photoelectric threshold, for films with thicknesses less than 2.5 nm, can be due to a particular profile of electronic density in small discrete islands.

The second minimum is observed for the critical thickness $d_0 = 7.5$ nm. This is an intermediate thickness between the granular films and the lacunar ones. Between a granular film and a lacunar one of neighboring mass thicknesses the surface value of deposit is totally different. Now, in the case of low-energy photoemission, Mahan[27] has shown that the surface must be taken into account. The work function splits up into several terms[28] and one of them depends on the electronic double layer on the surface. The surface of a metal is made up of the last row of ions. The dissymmetry thus introduced into the bulk potential must therefore be taken into account, as is done for example by Langreth.[29] In the neighborhood of the surface the density of charges is not the same as in the bulk, as is indicated by the calculation of Appelbaum and Hamann.[30] There follows a new distribution of charges having a maximum probability of being present at a distance X from the theoretical surface. All these ions and electrons, having charge centers which do not coincide, constitute an electronic double layer on the surface. The emitted photoelectrons cross this double layer and the corresponding energy intervenes in the calculation of the work function. The distribution of electronic densities can be calculated by means of different basic hypotheses, as is shown in the works of Bennet and Duke,[31] Lang,[32] Levin, Liebsch, and Benneman,[33] and Rawling and Reiss.[34]

The variation of mass thickness and therefore of macroscopic structure brings on a modification in the size of the surface in relation to the size of the bulk. This modification is particularly great in the neighborhood of the critical thickness d_0. It brings on a change in the distribution of charges in the neighborhood of the surface, and consequently, the variation of the distance X and the work function Φ.

C. Work functions and electric fields

A certain amount of results obtained by setting an external electric field to work on a metal cannot be interpreted according to Schottky's theory. The explanations put forward are generally of two types. Gumnick and Juenker,[35] for example, suggest presence of impurities to explain the anomalies observed with tantalum. In another context, Yang and Yang[36] take into account, besides the image force, exchange and correlation forces to interpret the periodic deviations shown by Stafford.[37] These explanations are not appropriate here; the metal studied is pure and we have not observed periodic deviations.

It seems interesting to interpret our results starting from a disturbance of the distance X previously defined. Thus, Theophilou and Modinos[38] have taken into account the variation of the potential barrier under the action of an electric field; Lang and Kohn[39] have calculated the electronic energies induced by an external field. When this is zero, the electronic double layer on the surface creates an electric field $\vec{E}_S^0$. When an external field $\vec{E}$ is applied, there ensues a rearrangement of this double layer: the field $\vec{E}_S$ takes on a new value $\vec{E}_S^1$ which compensates the effect of the external field. This variation of $\vec{E}_S$ brings on a variation in the energy needed by the photoelectrons in order to cross the double electronic layer. It is therefore understandable that effects due to the electric field or the structure are comparable, as they both act on a same physical quantity linked to the presence of a surface of the solid.

VI. CONCLUSION

With thin films of strontium deposited on an insulator substrate, we have studied the effect of the macroscopic structure and the action of an electric field of correct orientation applied perpendicularly to the film. The mass thicknesses, by means of which the structure of the thin films can be elicited, are within a range of 0.5–33 nm. The electric fields applied reach 985×10^3 V m^{-1}.

The variations of yield as a function of structure, when the films change from a granular deposit to a lacunar and then a quasicontinuous one, exhibit two peaks for thicknesses of approximately $d_1 = 2.5$ nm and $d_0 = 7.5$ nm. These peaks are considerable as the yield of a film approximately 2.5 nm thick is 10 times greater than the yield of a thick film ($d > 12$ nm). The corresponding variations of work function exhibit two minimums for thicknesses d_1 and d_0. For films thicker than 12 nm, the work function Φ is constant and equal to 2.64 eV. The first minimum is probably linked to the advent of conduction in the granular deposits. It should be observed that the thickness d_0 is intermediate between granular deposits and lacunar ones.

In every case, an external electric field applied perpendicularly to the film involves an increase of yield, which corresponds to a decrease of work function. The greater the field, the greater is this decrease. For a given film this decrease is proportional to $\sqrt{E}$, but the slope of representative straight lines does not generally corroborate Schottky's relation and varies according to the structure of the film. The difference $\Delta\Phi_E = \Phi_E - \Phi_0$ is greater or lesser according to this structure. The function $\Delta\Phi_E = f(d)$ has two minimums for thicknesses d_1 and d_0.

The analogy of the curves $\Phi = f(d)$ and $\Delta\Phi_E = f(d)$ shows that it should be possible to give an interpretation of this set of results starting from the disturbance of a single characteristic of the solid. This characteristic could be the electronic double layer on the surface. This layer is susceptible to modification by a change in the extent of the surface in relation to that of the volume, and equally by the action of an external electric field.

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