Thickness-Dependent Effects in the Work Function of Polycrystalline Cu-Films.

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Abstract. – Ideal metallic films are expected to show a thickness-dependent work function at a level of 0.1 eV in a short thickness range (5 nm). We investigated the variation of the work function with film thickness during the evaporation of polycrystalline Cu films on glass and Ni substrates, using the vibrating capacitor (Kelvin-)method. An increase of the work function with increasing film thickness at 0.1 eV level has been observed at the vacuum-metal interface according to the theoretical expectations. The effect, however, ranges over large thicknesses ($(10 \div 15)$ nm), *i.e.* comparable with electronic scattering lengths in metal films. This behaviour can be attributed to the violation of local charge neutrality in films with unlike surfaces.

1. Introduction.

The problem of an electron gas confined in a potential well has been often and sometimes contradictorily discussed in the literature.

A single-electron approximation using Dirichlet boundary conditions leads to a thickness-dependent Fermi wave vector, k_F:

$$k_F(d) = k_F(\infty) + O(1/d) + O(1/d^2), \tag{1}$$

with

$$O(1/d) = (1/d) \cdot (\pi/4 - \langle \eta \rangle_F),$$

$k_F(\infty)$ the Fermi wave vector of the bulk electron gas, d the film thickness and $\langle \eta \rangle_F$ the sum of surface-induced phase shifts for the wave functions.

The Sugiyama phase sum rule for thin films [1, 2], however, states that the sum of the surface-induced phase shifts equals $\pi/4$. Therefore the long-range term $(1/d)$ in eq. (1) disappears and local charge neutrality is obtained up to the order of $(1/d^2)$. This phase sum rule, however, strictly results only for films with symmetric surfaces [2].

Within the framework of single-particle Schrödinger equations, realistic charge densities

can be exactly calculated with self-consistent methods including many-body effects (Lang-Kohn formalism [3]). The calculations of Schulte [4, 5] for very thin films with symmetric surfaces demonstrated again the existence of local charge neutrality to the order of $(1/d^2)$.

Consequently for ideal films with symmetric surfaces there are no reasons to suspect a violation of the local charge neutrality, except the short-range terms in $(1/d^2)$. This conclusion is contrary to a recent discussion given by Rogers, Feuchtwang and Cutler [6].

Following eq. (1), the work function Φ of thin films should increase with increasing film thickness, since [3]

$$\Phi = \varphi(+\infty) - E_F, \tag{2}$$

where $\varphi(+\infty)$ is the electrostatic potential in vacuum.

These effects are at 0.1 eV level and of short range (5 nm) [4].

The problem of films with unsymmetric surfaces is still unsolved both from the theoretical and the experimental point of view. Realistic, supported films, however, rather correspond to unsymmetric systems. This unsymmetry can be produced for instance by unsymmetric potential wells due to an adsorbate layer at one film interface or by a double-layer metal film with different charge densities. It can be expected that a «sum rule» cannot be fulfilled to the same order as for ideal symmetric systems, i.e. additional correction terms to the work function even in $(1/d)$ might appear.

Only a few experimental results relating to a thickness-dependent work function observed under UHV conditions have been reported in the literature.

One group of authors [7, 8] observed at the metal-vacuum interface an increase of the photoelectric work function with increasing film thickness. The effects were at $(0.1 \div 0.2)$ eV level and restricted to the 5 nm thickness range. The accuracy of the experimental values, however, was limited to about 50 meV for film thicknesses smaller than 10 nm. These authors attributed the observed effects to the irregular island structure of their films.

In 1974, however, Wojciechowski [9] emphasized that these effects can be discussed with simple relations, i.e. like the $(1/d^2)$ term of eq. (1).

Another group of authors [10, 11] observed an increase (up to a factor 30) of tunnelling conductivity in MIM-structures with increasing thickness of one of the tunnelling electrodes. This effect can be attributed to a drop of the work function at the *opposite* of film-vacuum interface due to increasing film thickness. The observed effects were again at $(0.1 \div 0.3)$ eV level but have been of long range, comparable with the electronic scattering length $((10 \div 20)$ nm). Consequently, the observed effects were attributed to a violation of the sum rule in films with unsymmetric surfaces [11].

In this work we investigated the thickness-dependent work function at the metal-vacuum interface. The contact potential difference (CPD) [12a] was monitored *in situ* during the evaporation. The main advantage of this approach is evident: the measurement can be only performed if the thin film under discussion is electrically continuous.

2. Results.

The contact potential difference (CPD) was measured using the vibrating capacitor method (Kelvin method) [12a].

The vibrating electrode (electromagnetically driven pendulum) consisting of a 20 mm × 8 mm molybdenum sheet plated with 300 nm Au oscillates in front of the film substrate at a separation of 0.5 mm. The resonance amplitude was sufficiently large to expose the films substrate (15 mm × 6 mm) to the evaporation beam. The experiments have

been performed in UHV system (base pressure $5 \cdot 10^{-10}$ mbar), containing two evaporation sources. Essential experimental details of the computer-controlled evaporation process were already described in ref. [13].

Cu films on glass substrates.

The film substrates (fire polished Corning 7059) were thoroughly cleaned and subsequently heated in UHV at 500 K for some days.

Figure 1a) shows a typical dependence of the work function monitored during the evaporation of a Cu film on Corning glass kept at 300 K.

Prior to the fact that the film reaches electrical continuity, the contact potential difference shows an arbitrary value. The observed steep decrease of $\Delta\Phi$ at about 3.5 nm film thickness is produced by the coalescence of the film. Thereafter the feedback compensates the contact potential between film and reference (gold) electrode. This point was arbitrarily marked to $\Delta\Phi = 0$ in fig. 1a).

At films thicknesses larger than about 4.2 nm an increase of the work function ($\Delta\Phi = -\Delta(\text{CPD})$ [12a]) with increasing film thickness can be observed. The effect is at about 0.15 eV level, approaching a saturation value at a thickness of about 15 nm.

A qualitative discussion of the effect described above can be performed using the simple relations (1) and (2). Assuming that this long-range variation of $\Delta\Phi$ is only due to the
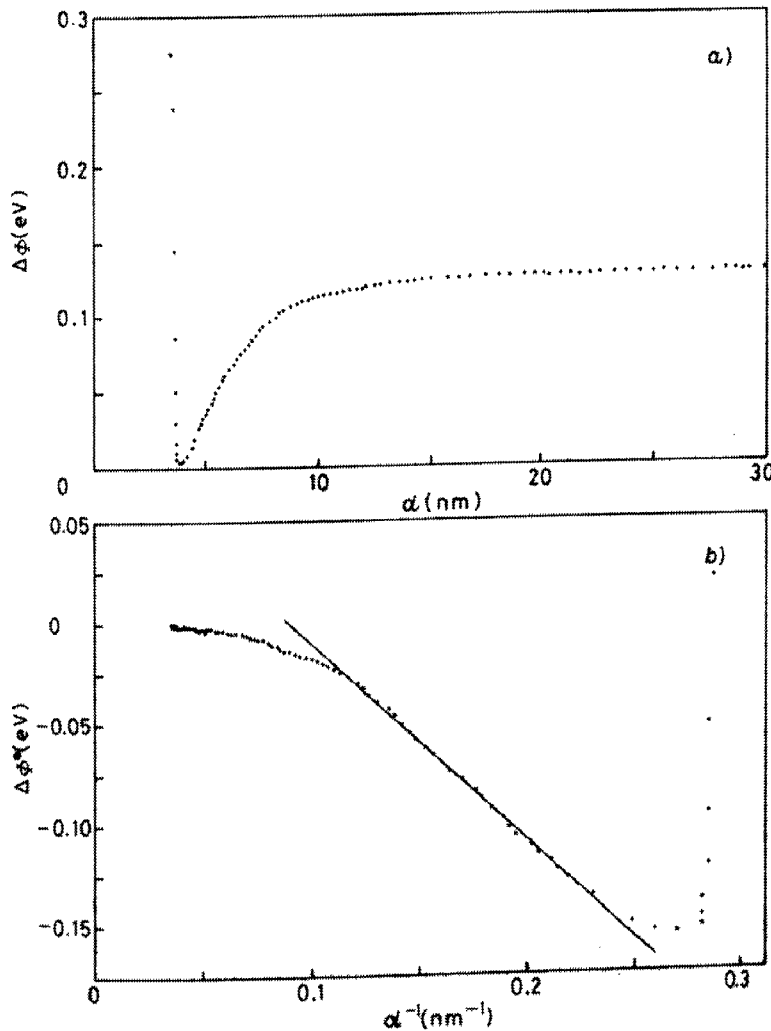

Fig. 1. – The observed thickness dependence of the work function of copper films on Corning glass. a) $\Delta\Phi$ vs. d; b) $\Delta\Phi^* = \Delta\Phi(d) - \Delta\Phi(\infty)$ vs. $1/d$.

variation of k_F, one obtains

$$\Delta\Phi^* = \Delta\Phi(d) - \Delta\Phi(\infty) = -\alpha/d, \tag{3}$$

where α can only be determined experimentally as long as no theoretical expression of eq. (1) is available for unsymmetric films.

The result of fig. 1a) is given in a $(1/d)$ plot of fig. 1b); here, $\Delta\Phi(\infty)$ was replaced by the saturation value of $\Delta\Phi$.

In the thickness range between 4 to 10 nm a clear linear dependence can be observed. The slope of the straight line amounts to $\alpha \simeq 0.8\,\text{eV}\cdot\text{nm}$. For all investigated Cu films α ranged between 0.5 and 0.8 eV · nm. This, however, only represents a qualitative analysis: regarding many-body theories, both a variation of k_F and of the charge distribution at the film boundaries have to be taken into account. The resulting thickness dependence of the work function should therefore be correctly calculated in a self-consistent way.

The analysis above shows qualitatively that local charge neutrality in the investigated Cu films seems to be violated, i.e. the sum rule cannot be fulfilled to the order of $(1/d^2)$ as expected for ideal (symmetric) films.

Cu *films on* Ni *substrates.*

The correlation of the thickness-dependent work functions at the two limiting surfaces of a thin film gives an additional information concerning the origin of the observed size effect.

The change in the work function on the opposite film surface (substrate side) shows an opposite sign, too [10, 11]. A thickness-dependent tunnelling conductivity was only observed if the films under discussion were condensed on a metal substrate covered with an adsorbate layer [10, 11]. The equivalent of these experiments for the vacuum-metal interface is presented in fig. 2.
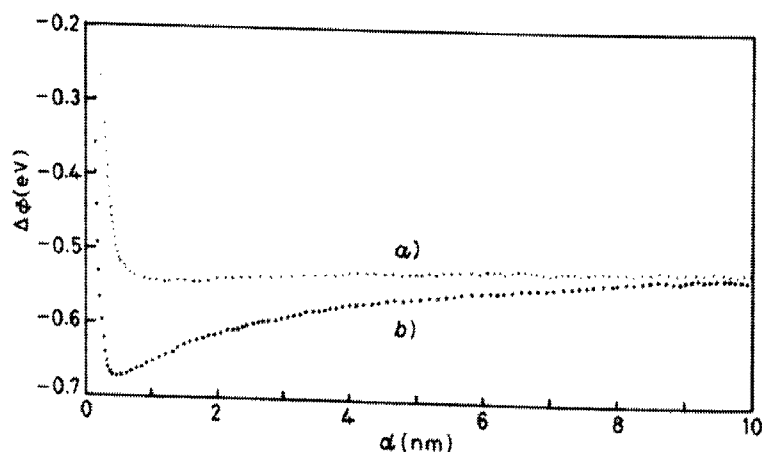

Fig. 2. – The observed thickness dependence of the work function of Cu cover layers on Ni substrates: a) Cu on clean Ni surface; b) Cu on contaminated Ni surface.

The substrate consists in a thick (100 nm) Ni film evaporated on Corning glass in the manner discussed above.

Curve a) of fig. 2 shows the thickness dependence of $\Delta\Phi$ for a Cu cover layer deposited immediately after the nickel substrate was evaporated. The value $\Delta\Phi = 0$ marked in fig. 2 represents the CPD of this nickel substrate.

The Cu cover layer becomes continuous at a thickness of about 0.8 nm. The following

increase of the Cu film thickness gives rise only to a constant value of $\Delta\Phi \simeq -0.52\,\text{eV}$ corresponding to the known difference $\Phi_{Cu} - \Phi_{Ni} = -0.5\,\text{eV}$ ($\Phi_{Cu} = 4.65\,\text{eV}$, $\Phi_{Ni} = 5.15\,\text{eV}$) for polycrystalline bulk metals [12b].

Curve b) of fig. 2 shows the thickness dependence of $\Delta\Phi$ for a Cu cover layer on a Ni substrate stored 40 hours in $10^{-9}\,\text{mbar}$.

The work function of the Ni substrate decreased during this time by $\Delta\Phi \simeq -0.3\,\text{eV}$, referring to the presence of an adsorbate layer on this surface, as already reported in the literature: $\Delta\Phi \simeq -0.6\,\text{eV}$ for Ni(100) [14] and $\Delta\Phi \simeq -0.4\,\text{eV}$ for Ni(110) [15] surfaces was observed during exposure to oxygen.

The thickness dependence of the cover layer-work function (curve b) of fig. 2) now shows the general behaviour of Cu films deposited on Corning glass, i.e. at 0.15 eV level and about 100 nm thickness range.

The result presented in fig. 2 clearly shows the influence of unsymmetric film surfaces on the thickness dependence of the work function. In the absence of adsorbate layers, no steep potential step occurs at the interface, since Ni and Cu have comparable electron densities. Therefore the double layer approximately acts as a thick single-layer film. On the contrary, the presence of an adsorbate layer generally produces a strong decrease of the electron density at the Cu-Ni interface. The system will be therefore highly asymmetric. The result of this asymmetry is evident: a thickness-dependent work function of long order will be observed.

The correspondence with the already observed decrease of the work functions on the opposite film margin (substrate side) [11] will also be clear: their changes should be of opposite sign in order to maintain the global charge neutrality of the system.

3. Discussion.

A thickness-dependent work function has been observed at the metal-vacuum interface of polycrystalline Cu films.

We observed a gradual increase of the work function with increasing film thickness at 0.1 eV level as expected from the theory. Contrary to the theoretical expectations, this effect is not limited to the 5 nm thickness range, but to thicknesses comparable with electronic scattering lengths in metal films [16, 17]. We therefore conclude that real (supported) thin films are rather unsymmetric. This unsymmetry gives rise to a violation of local charge neutrality, which naturally has to be accepted for ideal symmetric films.

Some experimental arguments supporting this hypothesis can be given:

Cu films on glass substrates show a $(1/d)$-dependence of the work function. This effect can theoretically be expected only if the local charge neutrality is violated. Otherwise a $(1/d^2)$-dependence should be observed.

Cu films on Ni substrates show a thickness-dependent work function only in the presence of an adsorbate layer at the Cu-Ni interface. This adsorbate layer gives rise to a strong decrease of the electron density at this interface, i.e. to a highly unsymmetric thin film system.

The thickness dependence of the work function on the opposite film surface (substrate side) is of the same order of magnitude but of changed sign (tunnelling experiments [10, 11]). This experimental evidence can be only explained in the presence of unsymmetric systems. On this way the global charge neutrality of the system will be conserved at each film thickness.

The problem of phase sum rule in films with unsymmetric surfaces was not treated up to now. Some marginal remarks, however, have been made by Appelbaum and Blount [2]. They stated that in the absence of symmetry additional arguments are to be used in order to obtain «sum rule». This, *i.e.* local charge neutrality, can be obtained if the charge neutrality in the middle of the film is conserved.

Unsymmetric potentials, however, give rise to an additional electrical dipole [2] which is to be annihilated in order to conserve the global charge neutrality of the system. A naive analysis emphasizes the complexity of this problem: if the charge density distribution at the two limiting boundaries is imposed to be perfectly symmetric, then no neutrality at the middle of the film can be obtained. Inversely, if this neutrality is imposed, the charge density distribution at the limiting boundaries will not be symmetric.

The theoretical situation is certainly more complex as discussed above. A self-consistent Lang-Kohn [4, 5] or a minimizing Rayleigh-Ritz analysis [18] of a double-layer problem would be more suitable.

On the other hand, unavoidable error sources arising from possible structural changes of the film surface during the growth of polycrystalline film were not discussed here. Nevertheless the presented results show physical consistency. The correlation with results of the thickness-dependent tunnelling conductivity, where such structural effects are not involved, provides the most effective argument for the consistency of the results presented above.

Efforts concerning both systematic investigations of thickness-dependent work functions and their theoretical interpretation are in progress.

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