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The Structure of Metal Films and the Changes in Their Conductivity During Adsorption

I. Adsorption of Water Vapor on Copper

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The effect of the adsorption of water vapor on the conductivity of thin copper films has been investigated, the films being obtained by vacuum evaporation and condensation on a glass support at different temperatures. It has been found that the effects observed strongly depend on the structure of the resulting metal film. This is explained by a proposed mechanism for electrical conduction in the thin metal films.

I. INTRODUCTION

There are only a few publications concerning the effect of the adsorption of water vapor on the conductivity of thin metal films. Suhrmann (*1*) considered that the water molecule plays a donor role in adsorption due to the free electron pairs on the oxygen atom. According to this author this should cause an increase in the conductivity of the films. Our investigation (*2*) on the effect of water vapor on the conductivity of thin silver films clearly showed such a reversible increase in conductivity. The interaction of water vapor with iron films is of a different kind (*3*). It has been established that adsorption of small amounts of water vapor on the iron surface leads to decomposition of the water and to evolution of hydrogen. This process is accompanied by a decrease in conductivity of the metal film. As a result, the iron surface is modified and subsequent amounts of vapor lead to a partly reversible increase in resistance without hydrogen release. It is supposed that in this stage of the process OH groups are formed on the metal surface. Later Suhrmann *et al.* (*4*) came to analogous conclusions. In some recent work, these authors (*5*) investigated the effect of the adsorption of H_2O vapor on the conductivity of copper films and found that there are no principal differences in the interaction between H_2O vapor and the surfaces of iron, nickel, and copper.

The present investigation was performed to obtain data on the adsorption of H_2O vapor on thin copper films with different structures and so to clarify, as far as possible, the role of structure on the effects observed.

II. METHODS

The thin copper films were obtained by condensation of electroscopically pure copper (99,99) in a glass evaporating cell of the type used by Suhrmann and Schulz (*6*). A small glass plate was placed in the same cell. At the end of each experiment the copper film deposited on the plate was studied by electron microscopy and an electron diffraction picture was obtained. A platinum–carbon replica was prepared from the film for electronmicroscopic observation. The experiments were carried out in an ultrahigh vacuum system at a pressure of the order of 2.10^{-9} Torr. The temperature of the support was kept at 77, 293, or at 600°K. During the evaporation in the last two cases the pressure increased but never exceeded 2.10^{-8} Torr. The gravimetrically measured thickness of the films varied from 30 to 2000 Å. Evaporation was carried out for 0.5 hr, from a point source, so the thickness of the film over the spherical cell is expected to be quite homogeneous. The film obtained was kept at constant room temperature for about 1 hr until a constant value of resistance was attained. This was necessary for further observations of the effect of water vapor. The films obtained at 600°K were ready for experiment immediately after they had reached room temperature. The resistance was measured by a direct current Wheatstone bridge, with an accuracy of 0.001 ohms. Adsorption was carried out at 293°K. Water vapor was produced in the system by fourfold distillation of gas-free water. The pressure was measured by a Bayard-Alpert ionization manometer IVM-05 and a thermocouple manometer LT-2. Oxygen was produced by thermal decomposition of potassium permanganate. The different parts of the system were separated from each other by gallium and membrane metal valves.

III. Results

The adsorption of H_2O vapor has different effects on copper films obtained at different temperatures (77, 293, and 600°K). We present the results from each case separately.

1. *Copper Films Obtained at 293°K*

Figure 1 shows the effect of adsorption of H_2O vapor on a comparatively thick copper film. The average gravimetric thickness was 500 Å. The changes of the resistance and the pressure are shown together in Fig. 1. As shown, the first small amount of H_2O vapor causes an irreversible decrease of resistance. (The adsorption of H_2O vapor is practically total.) No incondensable gas was detected. This means that the adsorption process is not accompanied by any release of gaseous products resulting from water decomposition on the copper surface. The second and third amounts admitted were greater. When a trap was immersed in liquid nitrogen (points A), there was still no uncondensable gas. The resistance decreased again, but the effect was fully reversible.

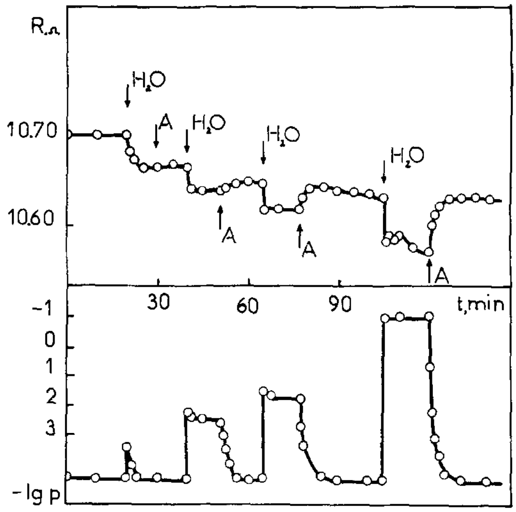

FIG. 1. Effect of the adsorption of H_2O vapor on the resistance of a pure copper film produced at 293°K; $d \approx 500$ Å. Temperature of adsorption measurements: 293°K.

Figure 2 shows the changes in conductivity of the same copper film with the

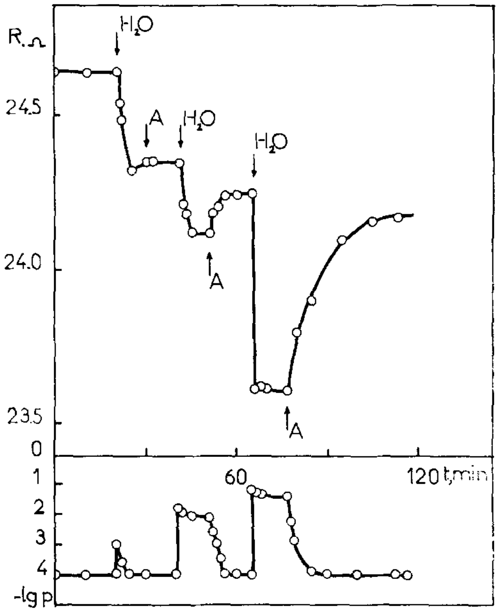

FIG. 2. Effect of the adsorption of H_2O vapor on the resistance of the same film as in Fig. 1. The resistance is measured between two other points.

same quantity of H_2O vapor adsorbed, but the resistance was measured between two other points of the film, the two pairs of points being situated in a small area of about 4 cm^2 on the surface of the film. As shown in Fig. 2, the effects are quite analogous, but the decrease in resistance is much greater. While in Fig. 1 for the first portion of water vapor, we obtained a relative change in resistance $\Delta R/R = 0.5\%$, in Fig. 2 for the same portion, the effect is twice as great, 1%. This fact is directly connected with the homogeneity of the thin metal layer. As said above, the film is considered to be homogeneous in regard to its gravimetric thickness. The experiments show that the adsorption of one and the same quantity of water vapor causes different effects on the resistance measured between different points on the surface of the film. Since this effect is strongly dependent on the effective thickness of the film (7) it may be concluded that the effective thickness of a given film depends on the direction of measuring. This shows that the notion "film thickness" is very limited, which makes difficult the experimental check of all quantitative dependences involving "film thickness."

If a comparatively thick copper film is partially covered with oxygen, the adsorption of water vapor has a different effect. As shown in Fig. 3, the adsorption of small quantities of vapor leads to an irreversible increase in resistance. The adsorption of greater quantities produces a decrease in resistance. If the copper surface is completely covered in advance with oxygen, water vapor causes only an increase in the resistance of the film. Moreover, the increase is comparatively slow and begins after a certain induction period. These results are shown in Fig. 4. Decrease in resistance is inherent only to the pure copper surfaces.

2. Copper Films Obtained at 600°K

The purpose of this thermal treatment was to obtain films of coarse grain structure.

Figure 5 illustrates the changes in the resistance of such a film in the case of adsorption of H_2O vapor at room temperature. As shown, the adsorption causes a considerable irreversible increase of resistance. The electronmicroscope study of this film showed orientation of the crystals predominantly in the plane (111). In this case, decrease in resistance is not observed.

In the case of thinner copper films with structural orientation, there is a more complex effect. The data in Fig. 6 show that for the first amounts of water vapor an increase and decrease vie with each other,

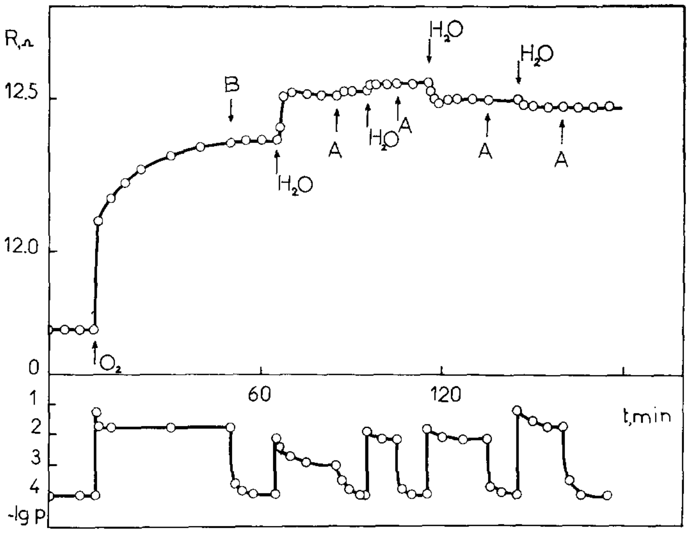

FIG. 3. Changes in resistance during the adsorption of H_2O vapor on a copper film partially covered by oxygen. Temperature of adsorption measurements: 293°K.

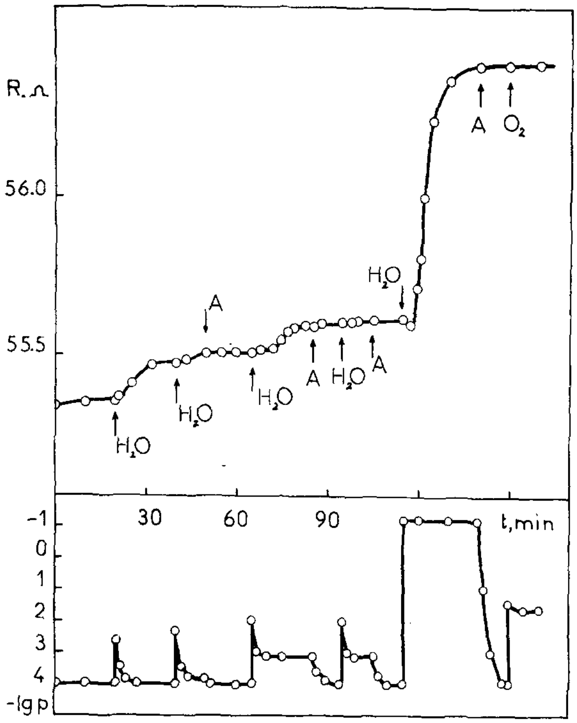

FIG. 4. Changes in resistance during the adsorption of H_2O vapor on a copper film fully covered by oxygen. Temperature of adsorption measurements: 293°K.

while after adsorption of considerable quantities of water vapor the effect of increase of the resistance prevails.

It is seen that the use of a film with coarse grain structure and with a particular orientation of the crystallites lead to a change in the observed phenomena. The difference cannot be attributed to a probable contamination of the metal film with oxygen in the course of thermal treatment, because the adsorption of H_2O vapor on copper film covered in advance with oxygen provokes other effects (see Fig. 3). It must be pointed out that coarse-grained copper films deposited at 600°K which exhibit no orientation display the same effects during water adsorption as the pure copper films deposited at 293°K.

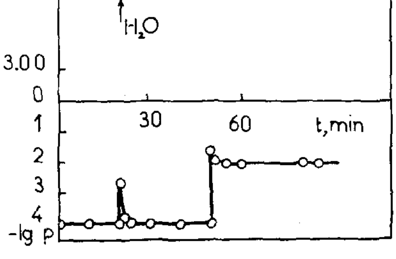

FIG. 5. Changes in resistance during the adsorption of H_2O vapor on a copper film obtained at 600°K with texture in the plane (111); $d \approx 2000$ Å. Temperature of adsorption measurements: 293°K.

3. Copper Films Obtained at 77°K

Using copper films deposited at 77°K, we observed an increase in resistance similar to that established by Suhrmann and co-workers. However, a process provoking a considerable decrease in resistance is also present: this is partially reversible and is compensated by the increasing effect. The decrease in resistance is clearly observed under desorption of H_2O vapor from the surface, which takes place when liquid-nitrogen trap is used.

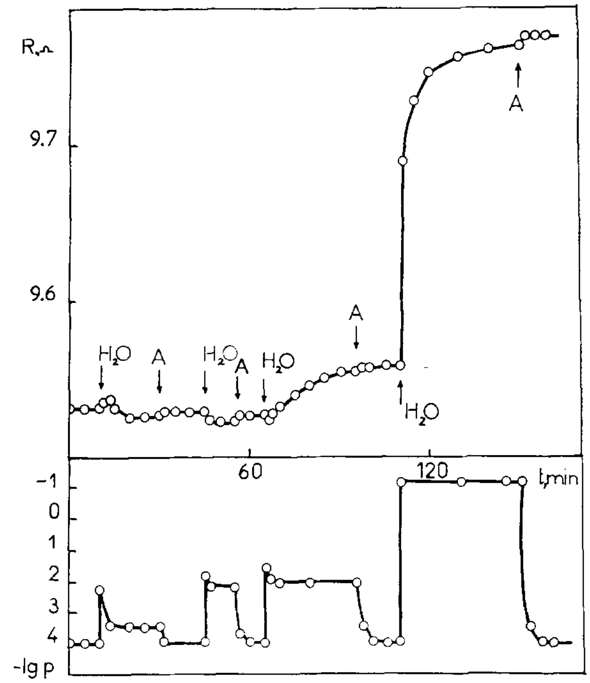

FIG. 6. Changes in resistance during the adsorption of H_2O vapor on a copper film obtained at 600°K with texture in the plane (111); $d \approx 1000$ Å. Temperature of adsorption measurements: 293°K.

The results from the adsorption on such a film with average thickness 300 Å are represented in Fig. 7. The first portion of H_2O vapor produces a small increase in resistance with a maximum. On the other hand, the desorption of H_2O vapor leads to a very pronounced increase in resistance. This means that the initial effect of increase in resistance is a resultant effect, due to the prevalence of the effect of increasing over the effect of decreasing of the resistance. The same effect is better manifested with the second admission of H_2O vapor. The admission of saturated H_2O vapor leads to a considerable increase in resistance. If the film so treated is subjected once more to the action of saturated H_2O vapor, only a reversible decrease in resistance is observed. The subsequent treatment of the same film with oxygen changes the character of the effects observed. The reversible decrease in resistance under the action of saturated H_2O vapor is not observed now, but a weak irreversible increase in resistance is present.

IV. DISCUSSION OF THE RESULTS

The experimental data show that the adsorption of H_2O vapor on thin copper films produces two effects on the resistance, namely an increase and a decrease.

The first is the common effect of adsorption of gases and vapors on the resistance of thin metal films. Water vapor is adsorbed irreversibly by the surface, it binds the metal atoms of the surface and thus produces a reduction in the effective thickness of the film. The resistance increases. The process is not connected with any observable decomposition of water. If, however, such a decomposition takes place, its products remain adsorbed by the surface. This is the difference between the surface of copper and the surface of iron or nickel, where the decomposition occurs with a release of gases.

The other effect is connected with the structure of the metal films. It may be ascribed to adsorption or condensation of H_2O molecules in the capillaries between the grains of the metal films. According to

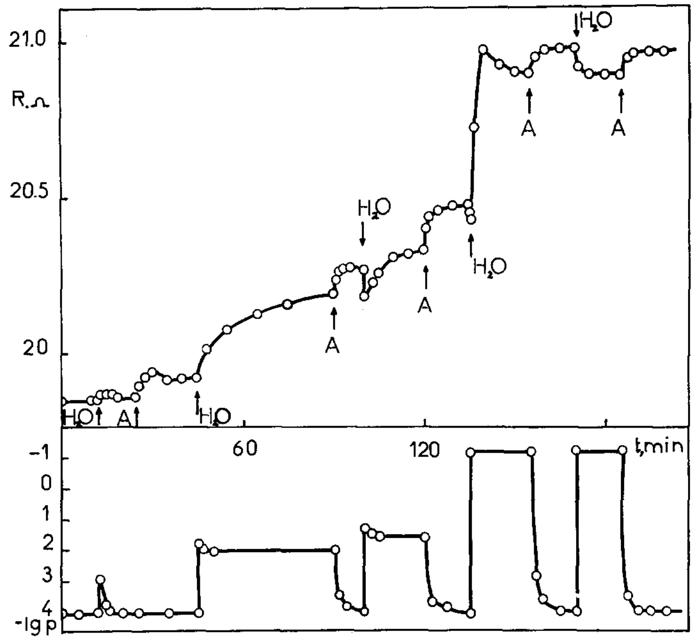

FIG. 7. Changes in resistance during the adsorption of H_2O vapor on a pure copper film obtained at 77°K. Temperature of adsorption measurements: 293°K.

Zwietering *et al.* (*8*), the metal film consists of many metal grains connected with each other by electrically conducting metal bridges. The resistance of these bridges determines the total resistance of the film. In fact, the mechanism of electrical conduction in the case of thin metal films is much more complicated. It is usually considered that electron transfer between the metal grains may occur also by tunnelling, by thermionic emission, by activated charge carrier creation, by substrate-assisted tunnelling, etc. (*9, 10*).

As shown in previous investigations (*11, 12*), the adsorption of mercury vapor produces a considerable decrease in the resistance of the film. This effect is attributed to the condensation of the vapor in the capillaries between the metal grains. It is probable that an analogous though less pronounced effect also takes place in the case of adsorption of water vapor. As water has a considerably lower conductivity than mercury, the process is not simply an increase of the thickness of the conductive bridges. It is known that the adsorption of water vapor on metal films reduces the work function (*5*). Probably, the adsorption of water vapor in the capillaries between the metal grains causes there a reduction of the work function in the same way. This would lead to an increase in the relative contribution of the emission mechanism for cases where the emission of electrons between the metal grains takes part in the total conductivity of the film.

Information about the structural differences of the metal films is furnished by the electronmicroscopic examination. The platinum–carbon replicas of films deposited at 600, 293, and 77°K show considerable differences in the dimensions and the shapes of the grains. The replica of the film obtained at 600°K reveals some structural orientation in the (111) planes. If films with commensurate resistances are compared, those obtained at 600°K are distinguished by their greater gravimetric thickness. Films about 1000 Å thick have a resistance of about 10 ohms. For the films obtained at 77 and 293°K this resistance corresponds to a less thick film (100–500 Å). This suggests that films deposited at 600°K have relatively thin metal bridges. In films obtained at 293 and 77°K, the gravimetric thickness for a given resistance does not differ greatly. The emission mechanism manifests itself by the temperature dependence of the conductivity. The films obtained at 293°K have a relatively low temperature coefficient of resistance, which suggests a considerable contribution of emission of electrons to the conduction.

The data as a whole suggest the models illustrated in Fig. 8 for the structures of the copper films obtained at 77, 293, and 600°K, respectively. Note that for the 600 and 77°K cases, the thickness of the metal bridges is considerably lower than the average gravimetric thickness of the film. It is supposed that the adsorption of H_2O vapor leads to a diminution of the effective thickness of the "bridges," which is connected with an increase of the resistance. The difference in the behavior of the two types of films is based on the greater distance which exists between the metal grains of the thermally treated films. For the latter, the emission mechanism does not take part in the electron transfer and a decrease in resistance is not expected on adsorption of water vapor. Such an effect, however, should be observed with films deposited at 77°K and should dominate with films obtained at room temperature because of the relatively thick metal bridges in that case (Fig. 8). The emission mechanism should cover a smaller fraction of the charge transport in films obtained at 293°K than in those obtained at 77°K. At the same time, the metal bridges of the former should be thicker. That is why the adsorption of water on such films should affect the conductivity by changing the work function, not by changing the effective thickness of the metal bridges. The experiments on the adsorption of H_2O vapor show that in thermally treated copper films only an increase in the resistance is observed, in those obtained at 77°K both the effects of increase and decrease in the resistance take place, while in the films obtained at room temperature only a reduction in the resistance occurs. When oxygen is pre-sorbed it inhibits strongly the emission mechanism and the reversible decrease in resistance is not observed.

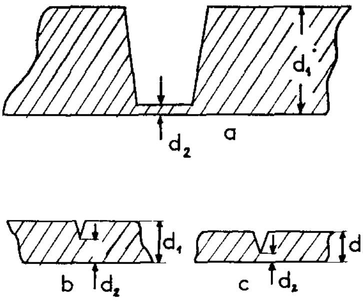

FIG. 8. A model representation of the differences in the structure of metal films obtained at: (a) 600°K; (b) 293°K; (c) 77°K. d_1 = the thickness of the film gravimetrically determined; d_2 = the thickness of the electrically conducting metal bridges.

The experimental data give reason to assume two forms of adsorption of water on copper, one of which is reversible and the other irreversible, although nothing can be said about the nature of the corresponding adsorption states. Depending on the structure of the film, the irreversible adsorption may provoke a rise or a decrease of resistance while the reversible one either decreases reversibly the resistance, or has no effect on it.

The difference in the behavior of textured and nontextured films should not be ascribed to the presence of texture, but to the structural changes in the film. The appearance of texture is to be regarded only as an indication of these changes.

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