NOTES

Influence of Oxygen Chemisorption on the
Thickness of Thin Silver Films

In 1960 Sachtler and Dorgelo (1) advanced the hypothesis that gas chemisorption on thin metallic films produces a decrease of their thickness of one to two atomic layers, due to the formation of a superficial complex between the metallic atoms and the adsorbed gas. This hypothesis explains the always positive experimentally observed variation of the electric resistance of metallic films during gas chemisorption.

Starting from Sachtler and Dorgelo's hypothesis and choosing the oxygen-silver system we aimed to evaluate the thickness decrease produced by chemisorption. To achieve this (a) we recorded the influence of chemisorbed oxygen on several electric properties depending on the film's thickness, such as electric resistance (2, 3), temperature coefficient of electric resistance (TCR) (4), and Hall tension (3); (b) we established quantitative relationships between the variations of these magnitudes and the thickness decrease due to chemisorption; (c) by using sufficiently thin silver films we were able to measure small changes in the above properties, changes which corresponded to a thickness decrease of about one layer of silver atoms.

The silver films thinner than 100 Å were deposited at the residual gas pressure of 10^{-8} torr on a glass support cooled to 77°K. After deposition the films were annealed in order to get stable structures with metallic conductivity, to which Fuchs's relation can be applied (5, 6).

During the oxygen chemisorption on such silver films we observed, in the temperature range of 77–273°K, an increase in the electric resistance (2, 3, 4) as well as a decrease in both TCR (4) and Hall tension (3).

In order to deduce the quantitative relations between the resistance increase ($\Delta R = R_1 - R_0$), respectively, the decrease in the TCR ($\Delta\alpha = \alpha_0 - \alpha_1$), and the thickness decrease ($\delta = d_0 - d_1$), we assumed at first that the variations observed were *entirely* produced by a decrease in the effective film thickness. We supposed furthermore that (1) the structure of the silver films was the same as in the bulk and did not change through oxygen chemisorption; (2) the electron scattering at the film surfaces was perfectly diffuse. By making use of Fuchs's simplified formulas applicable to films much thinner than the mean free path of the electrons in the bulk, l_∞ (6, 7), we found

$$\frac{\Delta\alpha}{\alpha_1} = \frac{\delta}{d_0} \qquad (1)$$

(valid in the range $d_0 \leq 0.15\ l_\infty$) for the decrease of TCR (4), and

$$\frac{\Delta R}{R_0} = \left[2 - \frac{1}{\ln(l_\infty/d_0)} \right] \frac{\delta}{d_0} \qquad (2)$$

(valid in the range $d_0 \ll l_\infty$) for the resistance increase (3). From (1) and (2) we obtained the following two values for the thickness decrease at saturation:

$$\delta_1 = (3.58 \pm 0.28)\text{Å} \qquad (3)$$

and

$$\delta_2 = (4.16 \pm 0.25)\text{Å} \qquad (4)$$

As can be seen, these values are in good agreement, their difference being noticeably smaller than two standard errors.

By comparing δ_1 and δ_2 with the lattice constant of the bulk silver, 4.0722 Å (8), it seems that the first superficial layer of silver atoms is involved in the oxygen chemisorption process.

As the electric resistance depends also on the number of conduction electrons, its increase during the chemisorption might be due *not only* to the thickness decrease but also to a change of this number. On basis of this assumption δ can be deduced from the following relation (4):

$$\frac{d_0}{d_0 - \delta} = \left(\frac{\alpha_0 R_1}{\alpha_1 R_0}\right)^{3/8} \tag{5}$$

(valid in the range $d_0 \leq 0.15\ l_\infty$). The thus found value is smaller than those obtained in the first case, but has the same order of magnitude:

$$\delta = (3.08 \pm 0.24)\text{Å} \tag{6}$$

It results therefore that even in this case there is an important influence of the thickness decrease on the electric resistance. As a matter of fact, our experimental data about the Hall tension behavior of thin silver films during oxygen chemisorption seem to indicate that the hypothesis of the thickness decrease is more probable than the hypothesis of the change in the number of conduction electrons (3).

In conclusion, we can say that our results concerning the influence of oxygen chemisorption on the electric resistance and on the TCR of thin silver films support qualitatively as well as quantitatively Sachtler and Dorgelo's hypothesis.

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Catalytic Hydrogenation by Dicyanobipyridinecobaltate (II) in Homogeneous Solution

In recent years, a number of metal complexes have been found (Co, Cu, Ru, Rh, Ag, Hg) which can activate hydrogen in solution (1–6).

From this published data, it is generally agreed that catalytic activity exists, if the catalyst has an unfilled d shell. In addition, as Schindewolf (7) pointed out, a complex compound must also be coordinately "un-saturated," in order that activation of hydrogen is possible. As such, with the ferrihexacyanide ion, in spite of the fact that it has an unpaired electron, no hydrogen absorption is observed, because it has six ligands (thus being coordinately "saturated").

Since, dicyanobipyridinecobaltate(II), Co(CN)$_2$Dip, first isolated by Cambi (8), has