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Electrical properties of chromium films

G. M. Abramova and G. S. Patrin*)

Krasnoyarsk State University, 660041 Krasnoyarsk, Russia

N. I. Kiselev and G. A. Petrakovskiĭ

L. V. Kirenskii Institute of Physics, 660036 Krasnoyarsk, Russia (Submitted July 17, 1998; accepted for publication September 3, 1998) Fiz. Tverd. Tela (St. Petersburg) **41**, 380–382 (March 1999)

We have investigated experimentally the influence of a constant electric current on the magnitude and temperature dependence of the resistance of chromium films prepared by vacuum-thermal condensation. The results are interpreted in terms of the Fröhlich conductivity model. © *1999 American Institute of Physics*. [S1063-7834(99)00303-2]

In recent years, coherent states of conduction electrons in solids have been received great interest, in particular, in the guise of the phenomenon of Fröhlich conductivity¹ observed in the slip region of charge density waves (CDW's) and spin density waves (SDW's) and manifested in the nonlinear growth of the conductivity in electric fields *E* larger than some threshold value E_c . For this mechanism, as follows from Ref. 2, the critical field E_c can be approximated by

$$eE_c(2\pi/Q) = (\Sigma^2/E_F)\varepsilon^4 10^6, \qquad (1)$$

where *e* is the charge of the electron, *Q* is the wave vector of the CDW (SDW), E_F is the Fermi energy, Σ is the dielectric gap of the CDW (SDW), and $\varepsilon \sim 1$. Estimates of the critical separation field of the spin density waves for chromium (Néel temperature $T_N \cong 312$ K, Ref. 3) based on Eq. (1) give $E_c \sim 16$ mV/cm. The critical separation current corresponding to E_c is given by

$$I_c = (l/R)E_c \,, \tag{2}$$

where *l* is the distance between contacts and *R* is the resistance of the metal. For bulk samples of chromium $R \sim 10^5 \Omega$ and for $l \approx 0.5$ cm the separation current $I_c \approx 800$ A. However, in chromium films the resistance *R* grows by several orders of magnitude as the film thickness is decreased.⁴ In view of this it may be expected that in chromium films for realistically attainable values of the transport current the Fröhlich conductivity regime is realized. For example, for $R = 50 \Omega$ one gets $I_c = 1.28 \times 10^{-4}$ A.

The present paper reports results of a study of the electrical properties of chromium films as functions of the transport current flowing through the sample.

Chromium films of thickness d=700 and 1040 Å were prepared by vacuum-thermal condensation on a glass substrate. The substrate temperature was T=180 °C. Electrolytic chromium of purity 99.99% or higher was used. The electrical resistance was measured by the four-probe potentiometric method at constant current in the temperature range T=77-350 K and current range $I=10^{-5}-10^{-1}$ A with an accuracy of $\pm 10^{-6} \Omega$. The temperature of the samples was monitored by a chromel-alumel thermocouple. The currentvoltage characteristics (CVC's) at T=78 and 300 K were measured in the fixed-current regime for the current in the range $I=10^{-5}-7\times10^{-3}$ A. The film thickness and its chemical composition were determined by x-ray fluorescence analysis, and the lattice parameters and phase composition—by x-ray structure analysis.

Figure 1 plots the temperature dependence of the resistance R(T), measured for different values of the constant current, for a chromium film of thickness d = 1040 Å. The points plotted in the inset for T = 78 K were taken from the CVC's. The results of the measurements of R(T) for $I = 10^{-3}$ A in the temperature range T = 200 - 300 K (inset to Fig. 1) agree with the data in the literature for thin chromium $films^4$ (d=14-50Å) and bulk samples.⁵ A weakly expressed anomaly in R(T) is observed in the region of $T_{an} = 280 \text{ K}$. Below T = 200 K the temperature dependence of the conductivity of the investigated chromium films differs substantially from that of the bulk samples,⁵ but is similar to that observed in chromium alloys (e.g., Cr-Fe and Cr-V, Ref. 6). It is clear from Fig. 1 that the magnitude and temperature dependence of the resistance of chromium films in the temperature region $T \sim 78$ K depends substantially on the magnitude of the current at which the measurements were made. For currents $I < 10^{-3}$ A, R(T = 78 K) exceeds R(T=300 K) by almost 10%. Thus, for $I=10^{-5} \text{ A}$ the ratio R(T = 78 K)/R(T = 300 K) = 1.095.

Figure 2 plots the dependence of the resistance on the transport current, calculated from the current–voltage curves. We found that the CVC's of the investigated chromium films at T=300 K obey Ohm's law up to $I\approx 4\times 10^{-2}$ A and are hysteresis-free. The R(I) dependence corresponding to the given current–voltage curve is plotted by curve I in Fig. 2. As follows from the experiment, the growth of the resistance at higher currents is associated with Joule heating of the sample. At T=78 K, as the current is increased the resistance falls abruptly in the current region $I=10^{-4}-10^{-3}$ A by almost 9% [curve 2 in Fig. 2(a)], after which a stepped falloff is observed up to $I\sim 10^{-1}$ A, with drops no greater than 1% [curve 2 in Fig. 2(b)]. The behavior of the CVC's and of R(I) did not depend on the polarity of



FIG. 1. Temperature dependence of the relative resistance $\delta(T) = R(T)/R(T=300 \text{ K})$ for different values of the transport current. *I* (A): $I = 10^{-4}$, $2 = 4 \times 10^{-4}$, $3 = 10^{-3}$, $4 = 7 \times 10^{-2}$. Inset plots the dependence $\sigma(T)$ for $I=10^{-3}$ A in the high-temperature region.

the current; however, hysteresis was observed in the "increase–decrease" current cycle. These results were reproduced in all succeeding experiments.

The experimental value of the current at which the abrupt drop in R(I) was observed was $I_J = 10^{-4}$ A. A smoother decrease in R(I) was observed up to $I = 3.4 \times 10^{-2}$ A, after which the resistance grew weakly and then remained constant up to $I \approx 10^{-3}$ A. Above this value a falling segment of R(I) is again observed [Fig. 2(b)]. The estimates based on Eq. (1) for the investigated films give the value $I_c = 6.8 \times 10^{-2}$ A, which is comparable with the experimental value I_J .

X-ray structure analysis of the films revealed the presence of an ultradispersed phase of chromium oxides. Chromium films with this type of phase composition, prepared by vacuum-arc sputtering, were discussed in Refs. 7 and 8. Note that quite a number of works have been dedicated to the problem of the formation of an oxide layer on the surface of chromium films (see, e.g., Refs. 7–9). According to the results of these works, the surface layer of the films consists of a mixture of metallic chromium and its oxides. The thickness of such a layer is equal to t=15-150 Å, depending on the method of preparation. The resistivity of the surface layer is given by the expression

$$(1/\sigma_0) = \rho_m^0 C_m^0 \{ 1 - (\mu_f / \mu_c)^n \}^{-1}, \qquad (3)$$

where ρ_m^0 is the resistivity of the metal, C_m^0 is the concentration of the metal in the layer, μ_f is the concentration of the oxide phase, and μ_c is the critical concentration of oxide for the percolation mechanism of conductivity; the parameter $n \sim 1-2$ (Ref. 8).

It is well known¹⁰ that, using four-probe measurement, the conductivity of the sample is given by

(

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_0 + \boldsymbol{\sigma}_v \boldsymbol{Z}. \tag{4}$$



FIG. 2. Dependence of the relative resistance $\delta(I) = R(I)/R(I=10^{-3} \text{ A})$ on the transport current. $I = 10^{-5} - 10^{-3} \text{ A}$ (a) and $10^{-3} - 8 \times 10^{-2} \text{ A}$ (b). T = 300 (1) and 78 K (2).

Here Z is depth into the sample, measured from its surface, σ_0 is the surface conductivity [in the given case it is given by formula (3)], and σ_v is the bulk conductivity. Since the thickness of the conducting layer in which the electric field and current density are still uniform is much larger than the film thickness ($t \sim 0.2$ cm, Ref. 11), it may be assumed that the entire volume of the film (d=1040 Å) contributes to the conductivity while the temperature dependence of the resistance is mainly determined by the conductivity of metallic chromium. This conclusion is supported by the dependence plotted in the inset to Fig. 1.

It was shown in Ref. 8 that the presence of a 15–20% oxide phase in Ni–Cr films increases the resistance twofold in comparison to the value characteristic of the metal. (Unfortunately, works dedicated to the electrical properties of chromium films have not indicated the value of the current at which the measurements were performed.) In our case, the resistance of the film at T=300 K, for a current $I=10^{-3}$ A, was $R=1.225\times10^{-4}$ Ω , which exceeds by two orders of magnitude the resistance of bulk samples of chromium.

Since at temperatures above the temperature of the resistance anomaly [Fig. 2(a)] no noticeable changes were observed in the resistance of the films, considered as a function of the current, the nature of the observed nonlinear effects in the low-temperature region can be associated with the presence of a SDW state, e.g., as a manifestation of Fröhlich conductivity due to slip of the spin density wave.¹

The experimental results obtained here allow one to conclude that the electrical properties of chromium films of the given thickness depend substantially on the magnitude of the transport current. To come to an unambiguous conclusion about the mechanisms responsible for the observed peculiarities in the electrical conductivity of chromium films, a detailed study of the dependence of the electrical properties on the conditions of preparation as well as the thickness is required.

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^{*)}E-mail: pat@iph.krasnoyarsk.ru

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