Unconventional drop in the electrical resistance of chromium metal thin films at low temperature

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Abstract

We studied the electrical resistance of single-crystal and polycrystalline chromium films. The $\rho(T)$ curve of single-crystal films decrease with decreasing temperature and show humps at around 300 K consistent with the bulk chromium being an itinerant antiferromagnet. In the polycrystalline films, on the other hand, the $\rho(T)$ curves deviate from those of the bulk chromium. Moreover, we observed sudden decrease in the resistance around 1.5 K. Although previous studies suggested that chromium films become superconductive (P. H. Schmidt et al., Physics Letters, **41A**, 367 (1972)), it is difficult to conclude whether a superconducting transition occurs because the electrical resistivity is not zero in all films. No anomaly was detected by resistance measurements around room temperature, and the sudden decrease in the resistance at low temperature may be attributed to the suppression of antiferromagnetic interaction by thinning down the chromium element.
Keywords: Cr film, sheet resistance, electrical resistivity, superconductivity

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1. Introduction

Since magnetic ordering and superconductivity apparently compete in conventional superconductors, some magnetic materials do not exhibit superconductivity. For example, iron (Fe) is a typical magnetic metal element that shows ferromagnetism at room temperature and ambient pressure. However, superconductivity is observed in Fe under high pressure between 15 and 30 GPa at 2K[1, 2]. Such behavior is related to the structural phase transition under pressure from the ferromagnetic bcc (α-Fe) phase to the paramagnetic hcp (ϵ-Fe) phase[3]. This idea is partially supported by examples in heavy fermion systems that exhibit superconductivity after suppression of magnetism to some extent under pressure[4, 5, 6, 7, 8].

Chromium, an antiferromagnet below the Néel temperature $T_{\mathrm{N}} = 311$ K[9] at ambient pressure, doesn't exhibit superconductivity even under pressure[1]. This may be attributed to the fact that T_{N} decreases with increasing pressure but tends to saturate. Such behavior can be explained by taking into account of a two-band model of itinerant antiferromagnetism[10, 11].

On the other hand, Schmidt *et al.* reported that thin films of chromium metal suppress the antiferromagnetic ordering and become superconductive at $T_{\mathrm{C}} \sim 1.5$ K, whereas there was no experimental data such as resistivity drop and the Meissner effect[12, 13]. It will be remarkable if chromium thin film exhibit bulk superconductivity, because it has not been reported for strongly correlated $3d$ transition-metal compounds such as Cr-based superconducting compounds, except for CrAs[14, 15]. In the present study, we perform precise electrical resistance measurements of chromium thin films to clarify the electronic state in a wide temperature range.

2. Experimental

Several polycrystalline chromium films were deposited on silicon substrate using ion beam sputtering with a base pressure of about 8×10^{-6} Pa. The working deposition gas was argon and a pressure was controlled between $1.15 \times$

10^{-2} and 1.17×10^{-2} Pa. Single-crystal chromium films were prepared using a conventional magnetron sputtering device in ultrahigh vacuum below 2×10^{-6} Pa[16]. The Ar pressure during deposition was 0.1 Pa. The substrate for growing chromium epitaxially (001) MgO. Since there are no capping layers in the same way of the previous reports, chromium oxide may exist on the surface. From the result of the X-ray reflectivity measurements, the thickness of the chromium oxide layer is obtained to be about 1 nm. The electrical resistance was measured by a four-point collinear four-probe dc method with the current direction on the film plane. Since the chromium oxide layer is uncongenial to the gold wires, aluminum wires were bonded on the film plane by wire bonding. The temperature dependence of the electrical resistivity was measured using the Quantum-Design PPMS between 0.5 and 350 K in the low-temperature laboratory, Kanazawa University. The direction of the applied field was perpendicular to the film plane and the electrical current.

3. Results and Discussion

Figure 1 shows the electrical resistivity $\rho(T)$ of single-crystal chromium thin film as a function of temperature between 0.5 and 350 K. At 300 K, ρ is 15.6 and 14.5 $\mu\Omega$cm for 200 nm and 400 nm thick samples, and both compare well with previous studies for bulk single-crystal chromium[17]. Both $\rho(T)$ curves decrease with decreasing temperature and show humps at around 300 K. This differs from the previous study of the chromium film[12], but is consistent with the fact that bulk chromium is an itinerant antiferromagnet with T_{N}[9, 10, 11] below which the incommensurate spin density wave is stabilized. Below T_{N}, no anomaly is observed in the $\rho(T)$ curve. The inset of Fig. 1 shows the $\rho(T)$ curve at low temperature below 60 K. While $\rho(T)$ of bulk single-crystal chromium shows a T^3 power low below 100 K[17], such behavior is not observed in those of single-crystal thin films. The slope of $\rho(T)$ curve of 200 nm thick sample is almost same as that of 400 nm thick one in a wide temperature range below 60 K, and $\rho(T)$ becomes almost constant below 15 K within the experimental

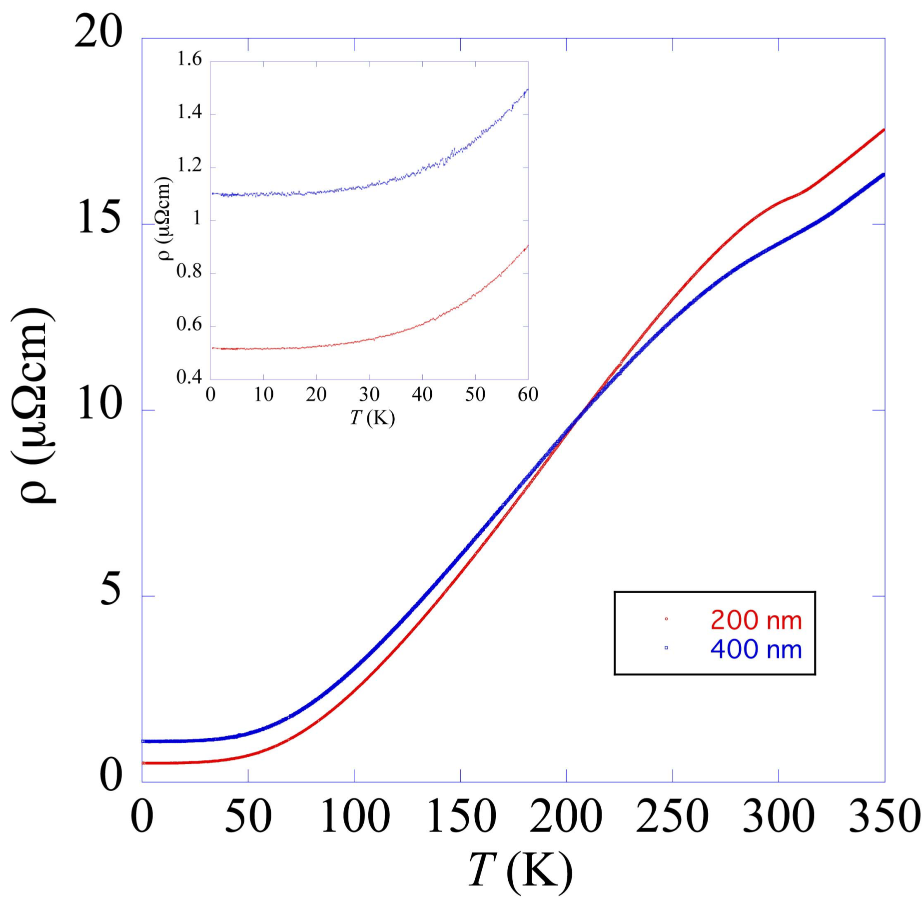

Figure 1: Electrical resistivity ρ of single-crystals chromium films as a function of temperature. Inset shows the $\rho(T)$ curve at low temperature below 60 K.

error. These results indicate that superconducting transition does not occur down to 0.5 K in single-crystal chromium films. It is strange that the residual resistivity ratio (RRR) of the 200 nm thick sample is larger than that of the 400 nm thick sample. From the results of the X-ray diffraction measurements, the lattice constant of the 200 nm thick sample is obtained to be 2.976 Å, which is almost same as 2.974 Å in that of the 400 nm thick sample. Such difference of RRR may come from the presence of impurities, defects, and strains in each thick films.

In polycrystalline films, on the other hand, the $\rho(T)$ value is much larger than that of single-crystal films. Because two-dimensional conductivity may be critical to the electrical resistance of polycrystalline films, we calculate the sheet resistance $R_s = RW/L$, where R is the electrical resistance of the film, and W and L are the width and length, respectively. The $R_s(T)$ curves in all polycrystalline chromium films differ from those of single-crystal films in Fig. 1 and bulk samples in previous studies[9, 10, 11]. First, no hump is observed around 300 K in the $R_s(T)$ curve, which is consistent with previous studies where a superconducting transition is observed[12, 13]. Second, semiconducting behavior is observed at low temperature in all films.

Figure 2 shows the R_s of 10 and 50 nm thick polycrystalline chromium films as a function of temperature between 0.5 and 350 K. In this figure, $R_s(T)$ increases monotonically with decreasing temperature. In Figure 3, we show the sheet conductivity $\sigma(T) = R_s(T)^{-1}$ as a function of $\ln T$. We found that σ is proportional to $\ln T$ below 10 K. The coefficient of the $\ln T$ term is 1.0×10^{-5} and $3.0 \times 10^{-5}\ \Omega^{-1}/\Box$ in 10 nm and 50 nm thick films, respectively. These values are close to $e^2/2\pi^2\hbar = 1.24 \times 10^{-5}\ \Omega^{-1}/\Box$ that is observed in two-dimensional disordered metals, which indicates that the localization and interaction effects of electrons in weakly disordered systems are important[18, 19, 20, 21, 22]. On the other hand, a metallic behavior is observed in the $R_s(T)$ curve of 50 nm thick film above 330 K. Similar behavior is often observed in doped semiconductors for impurity concentration varying from insulating to metallic range[23, 24, 25, 26]. For example, the electrical resistivity of carbon-doped GaAs shows a minimum above 100 K[25]. It means that scattering from phonons can be dominant at high temperature range even in semiconductors. Taking account that both absolute value of the R_s and the slope of $R_s(T)$ curve of the 50 nm thick film are much smaller than those of 10 nm one, it is reasonable to assume that scattering from phonons is more important in the $R_s(T)$ at high temperature than the localization and interaction effects of electrons.

For films thicker than 200 nm the $\sigma(T)$ curves deviate from the $\ln T$ dependence, and tend to saturate at low temperature. This indicates that three-dimensional conductivity of chromium metal may be critical to the electrical

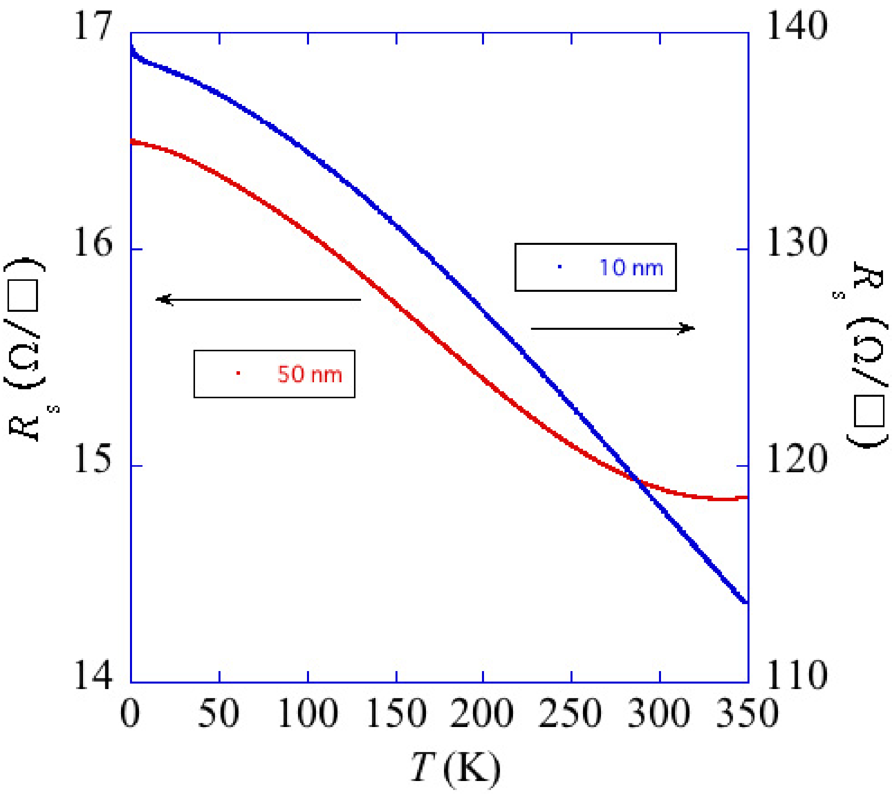

Figure 2: Sheet resistance R_s of chromium polycrystalline films of 10 and 50 nm thick as a function of temperature.

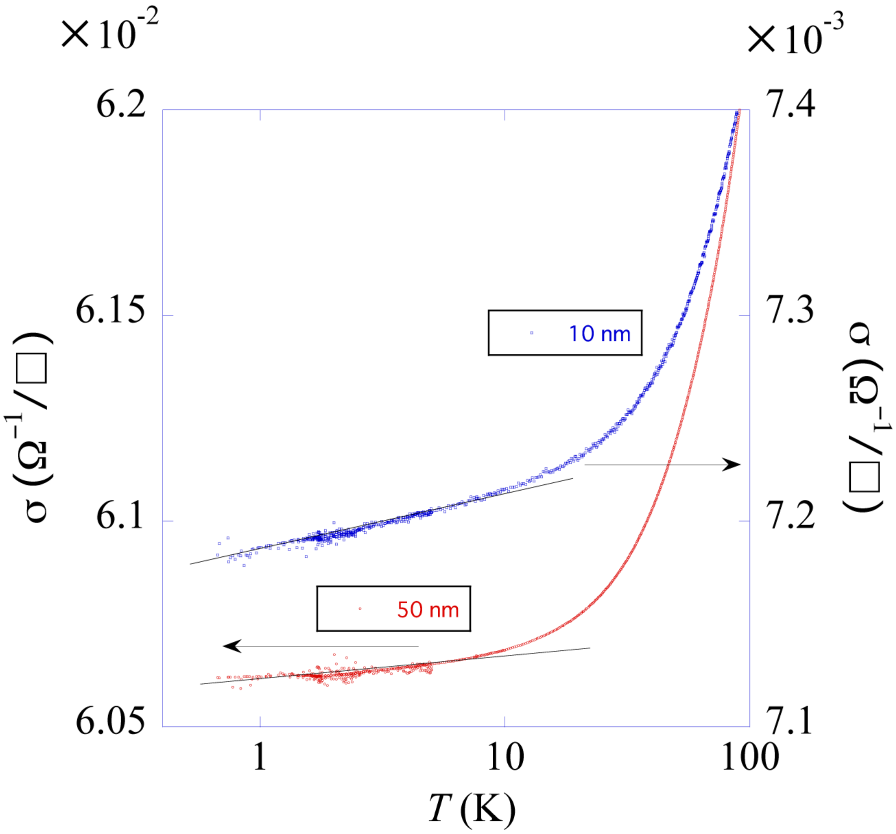

Figure 3: Sheet conductivity $\sigma(T) = R_s(T)^{-1}$ of chromium polycrystalline films of 10 and 50 nm thick as a function of $\ln T$. The straight solid lines emphasize the logarithmic behavior of $\sigma(T)$.

resistance. Figure 4 shows the electrical resistivity ρ as a function of the temperature for polycrystalline chromium films with thickness of higher than 200 nm. The $\rho(T)$ curve shows a minimum at $T_{\min} = 165$ K for the 200 nm thick, at 143 K for the 400 nm thick, and at 52 K for the 800 nm thick film, respectively. It is reasonable to assume that the minimum of the $\rho(T)$ curve is caused by the competition between the electron-phonon interaction at high temperature and the localization and interaction effects of electrons of two-dimensional disordered metals at low temperature. $T_{\min}$ decreases as increasing the thickness of film because the interaction effects of electrons of two-dimensional disordered metals are suppressed in the thick film. For the film of 800 nm thickness, a hump is observed around 150 K in the $\rho(T)$ curve. It is unclear whether such behavior is related to the magnetic properties of chromium films.

Figure 5 shows the normalized electrical resistance at low temperature in the zero-field cooling precess. We found that the resistance drops are observed at 1.5 K for 50, 200, 400 and 800 nm thick films. Although such behavior may correspond to previous studies[12, 13], it is difficult to conclude whether superconducting transition occurs since the electrical resistivity is not zero in all films. The magnitude of the resistivity drop ratio is very small, i.e., 0.01, 0.11, 0.11 and 0.04 % for the films of 50, 200, 400 and 800 nm thick, respectively. To examine the existence of hysteresis caused by pinned vortices trapped in the sample, the measurement of the electrical resistance in the field cooling precess is planed in future. In the 10 nm thick film, the resistivity drop is not observed down to 0.5K despite the small value of $R_s = 100\Omega/\Box$. This differs from the case of nonmagnetic metal films such as Sn and In, in which evolution from insulating to metallic superconducting behavior is observed with increasing thickness and decreasing sheet resistance nearly $h/4e^2 = 6.45$ k$\Omega/\Box$[27, 28, 29, 30].

Figure 6 shows the electrical resistance of the 200 nm film for the current of 10 μA and 100 μA. It is found that both $R(T)$ curves are almost the same and that the resistance drops are observed at same temperature. It means that Joule heat by an electric current doesn't affect the behavior of the electrical resistivity. The inset of figure 6 shows the current-voltage characteristics of

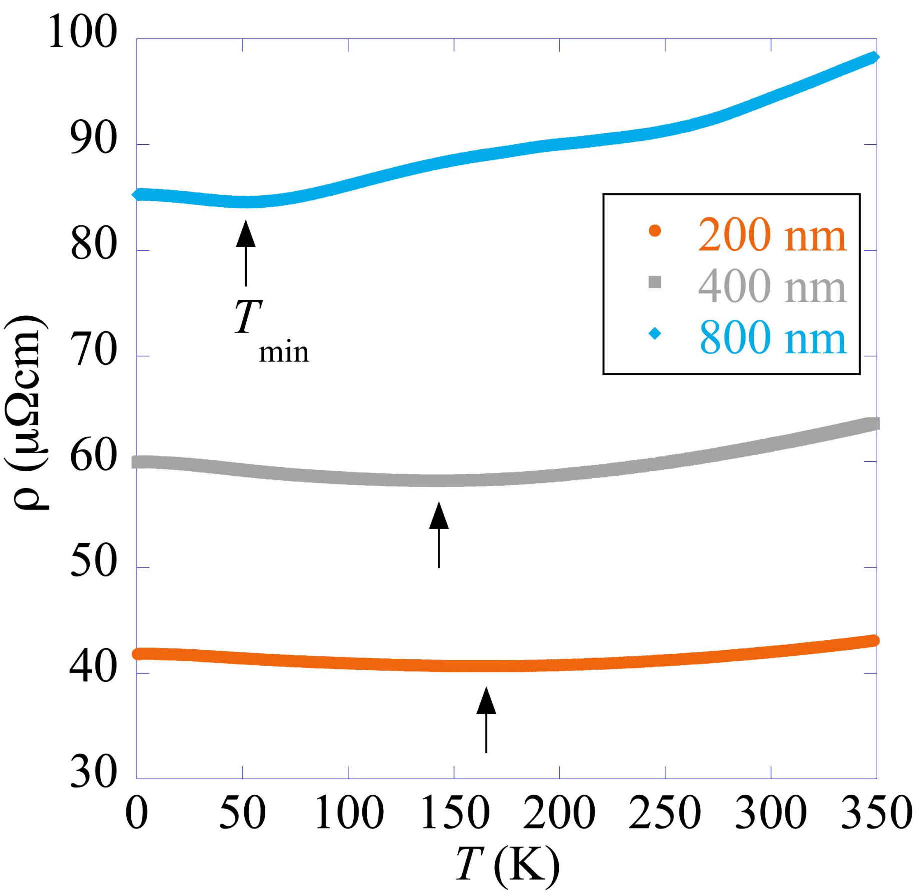

Figure 4: Electrical resistivity ρ of chromium polycrystalline films of 200, 400 and 800 nm thick as a function of temperature. The arrows indicate temperatures where $\rho(T)$ curve shows minimum.

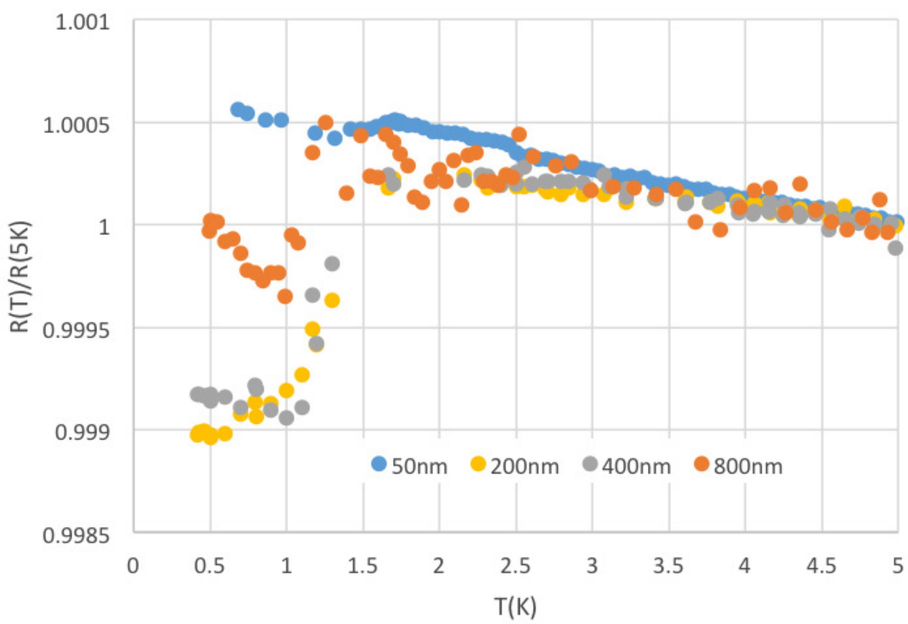

Figure 5: Electrical resistance of chromium polycrystalline films of several nm thick at low temperature normalized to their values at 5 K.

chromium polycrystalline films at 0.5 K. Ohmic resistance is observed within the error margin in the current region of the measurements between 100 nA and 1000 μA. No sign of the critical current is observed within the experimental error because the magnitude of the resistivity drop ratio is very small.

Figure 7 shows the magnetoresistance ratio MR of chromium polycrystalline thin film as a function of the magnetic field. Here the MR is defined as

$$\mathrm{MR}(B) = \frac{R(3\ \mathrm{kOe}) - R(B)}{R(3\ \mathrm{kOe})}$$

We found that the slope $d\mathrm{MR}/dB$ at 0.5 K is positive and the MR tends to saturate above 2 kOe. The change of MR is obtained to be 0.13 and 0.11 % for samples 200 nm and 400 nm thick, respectively, which is identical to the magnitude of the electrical resistivity drop, as mentioned in Fig. 5. No sign of the hysteresis is observed within the experimental error. Taking account of a magnetic background of the film and the substrate, it is difficult to obtain the upper critical field accurately. On the other hand, the MR curve is independent

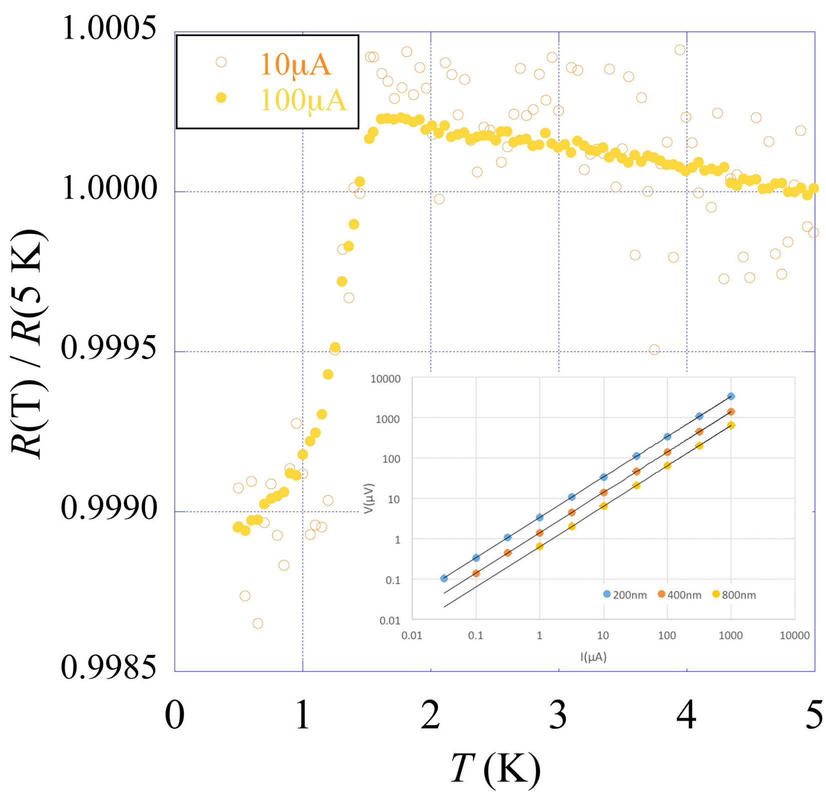

Figure 6: Normalized electrical resistance of chromium polycrystalline films of 200 nm thick for the current of 10 μA and 100 μA. Inset shows the log-log plot of the current (I) - voltage (V) characteristics of polycrystalline chromium films at 0.5 K. The solid lines correspond to $V \propto I$.

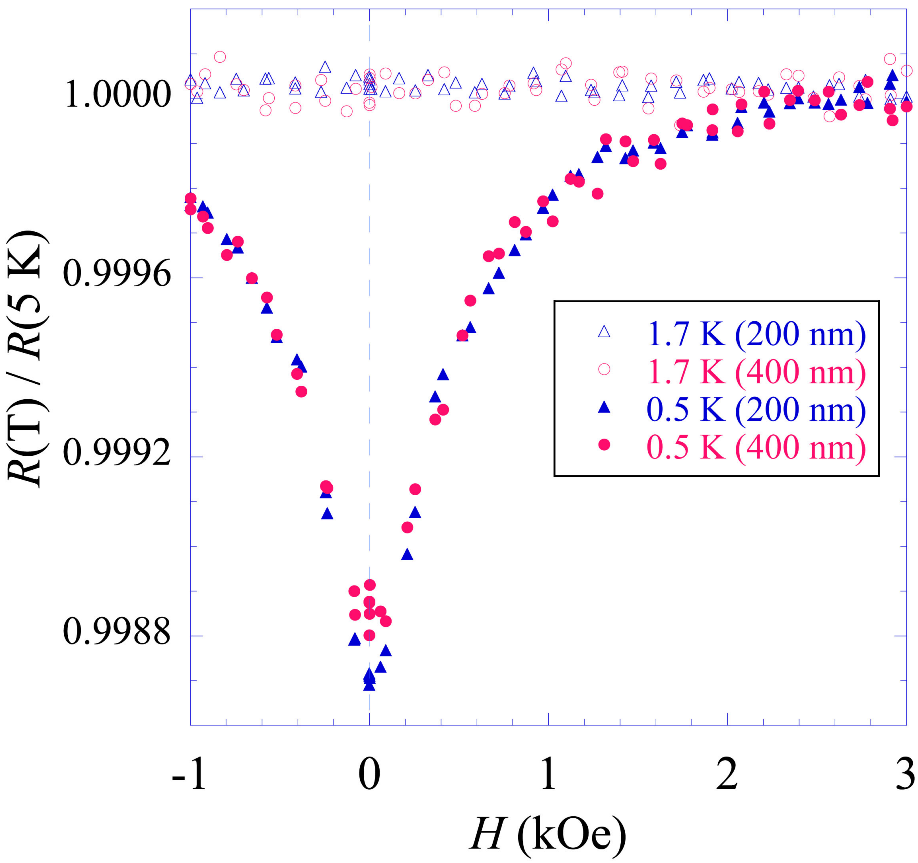

Figure 7: Magnetoresistance of chromium polycrystalline films at 0.5 K and 1.7 K.

on the magnetic field at 1.7 K. It indicates that the electrical resistance does not decrease below 1.7 K at a magnetic field above 2 kOe.

4. Summary

In this study, we performed the electrical resistance measurements on single crystals and poly crystals of chromium thin films. On the basis of a previous study investigating superconducting transition in chromium film, we attempted to analyze our data assuming that a superconducting phase exists at low temperature. Note that the large residual resistance remains even though the resistance drop is observed at 1.5 K where the superconducting transition was reported. It suggests that chromium does not show superconductivity contrary to the previous study. Possible factors are as follows. First, some chromium oxide may be produced on a film surface, and partially show a superconducting transition. Even in this case, exhibiting superconductivity is a remarkable because no Cr-based superconducting compound has been observed except for CrAs, as mentioned earlier. Second, taking into account that no transition is observed at 1.5 K in the single-crystal chromium films, another possibility is that crystalline impurities in chromium may be superconducting or show some magnetic transition. Third, taking account that T_C is enhanced in granular aluminum films[31], aluminum wires may create grains on chromium. To clarify the transport properties of polycrystalline chromium, more precise experiments are required at low temperature in detail. Several measurement of chromium films, such as capped one to avoid the oxidation or one bonded by another compatible wires which is not superconducting, is planed in future.

Acknowledgments

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References

[1] K. Shimizu, K. Amaya, N. Suzuki, Pressure-induced superconductivity in elemental materials, J. Phys. Soc. Jpn. 74 (5) (2005) 1345.

[2] K. Shimizu, T. Kimura, S. Fujimoto, K. Takeda, K. Kontani, Y. Ōnuki, K. Amaya, Superconductivity in the non-magnetic state of iron under pressure, Nature 412 (2001) 316.

[3] K. Takeda, M. Mito, Disappearance of bulk ferromagnetism of iron at high pressures above 9 gpa, J. Phys. Soc. Jpn. 71 (3) (2002) 729.

[4] Y. Uwatoko, I. Umehara, M. Ohashi, T. Nakano, G. Oomi, Handbook on the Physics and Chemistry of Rare Earths, Vol. 2, North-Holland, Amsterdam, 2012, Ch. 252, p. 1.

[5] T. Nakano, M. Ohashi, G. Oomi, K. Matsubayashi, Y. Uwatoko, Pressure-induced superconductivity in the orthorhombic kondo compound $CePtSi_2$, Phys. Rev. B 79 (17) (2009) 172507.

[6] H. Miyagawa, G. Oomi, M. Ohashi, I. Satoh, T. Komatsubara, M. Hedo, Y. Uwatoko, Electronic states of single crystal $CeAl_2$ near the pressure-induced quantum critical point, Phys. Rev. B 78 (6) (2008) 064403.

[7] M. Ohashi, G. Oomi, S. Koiwai, M. Hedo, Y. Uwatoko, Fermi-liquid instability of $CeRh_2Si_2$ near a pressure-induced quantum phase transition, Phys. Rev. B 68 (14) (2003) 144428.

[8] M. Ohashi, G. Oomi, I. Satoh, AC magnetic susceptibility studies of single crystalline $CeNiGe_2$ under high pressure, J. Phys. Soc. Jpn. 76 (11) (2007) 114712.

[9] W. C. Koehler, R. M. Moon, A. L. Trego, A. R. Machintosh, Antiferromagnetism in chromium alloys. i. neutron diffraction, Phys. Rev. 151 (2) (1966) 405.

[10] D. B. McWhan, T. M. Rice, Pressure dependence of itinerant antiferromagnetism in chromium, Phys. Rev. Lett. 19 (15) (1967) 846.

[11] M. Ohashi, G. Oomi, Simple experimental procedure under quasi-hydrostatic pressure up to 15 GPa at low temperature, Jpn. J. Appl. Phys. 48 (7R) (2009) 070221.

[12] P. H. Schmidt, R. N. Castellano, H. Barz, B. T. Matthias, Superconducting ion beam sputtered chromium metal thin films, Physics Letters 41A (4) (1972) 367.

[13] P. H. Schmidt, R. N. Castellano, H. Barz, A. S. Cooper, E. G. Spencer, Variation of superconducting transition temperatures of transition-metal thin films deposited with the noble gases, J. Appl. Phys. 44 (4) (1973) 1833.

[14] W. Wu, J. Cheng, K. Matsubayashi, P. Kong, F. Lin, C. Jin, N. Wang, U. Uwatoko, J. Luo, Superconductivity in the vicinity of antiferromagnetic order in CrAs, Nature Communications 5 (2014) 5508.

[15] H. Kotegawa, S. Nakahara, H. Tou, H. Sugawara, Superconductivity of 2.2 k under pressure in helimagnet CrAs, J. Phys. Soc. Jpn. 83 (9) (2014) 093702.

[16] Y. Sakuraba, J. Nakata, M. Oogane, H. Kubota, Y. Ando, A. Sakuma, T. Miyazaki, Fabrication of Co_2MnAl heusler alloy epitaxial film using Cr buffer layer, Jpn. J. Appl. Phys. 44 (9A) (2005) 6535.

[17] A. Yeh, Y. A. Soh, J. Booke, G. Aeppll, T. F. Rosenbaum, S. M. Hayden, Quantum phase transition in a common metal, Nature 419 (3) (2002) 459.

[18] P. W. Anderson, E. Abrahams, T. V. Ramakrishnan, Possible explanation of nonlinear conductivity in thin-film metal wires, Phys. Rev. Lett. 43 (10) (1979) 718.

[19] B. L. Altshuler, A. G. Aronov, Interaction effects in disordered fermi systems in two dimensions, Phys. Rev. Lett. 44 (19) (1980) 1288.

[20] S. Kobayashi, F. Komori, Y. Ootuka, W. Sasaki, ln T dependence of resistivity in two-dimensionally coupled fine particles of Cu, J. Phys. Soc. Jpn. 49 (4) (1980) 1635.

[21] F. Komori, S. Kobayashi, W. Sasaki, Spin-orbit interaction and electronic conduction in two-dimensional disordered metals, J. Phys. Soc. Jpn. 51 (10) (1982) 3136.

[22] F. Komori, S. Okuma, S. Kobayashi, Electron localization and interaction in thick metallic films, J. Phys. Soc. Jpn. 53 (5) (1984) 1606.

[23] E. Abramof, A. F. Silva, B. E. Sernelius, J. P. Souza, H. Boudinov, Transport properties of sillicon implanted with bismuth, Phys. Rev. B 55 (15) (1997) 9584.

[24] A. F. Silva, B. E. Sernelius, J. P. Souza, H. Boudinov, H. Zheng, M. P. Sarachik, Inpurity resistivity of the double-donor system Si:P, Bi, Phys. Rev. B 60 (23) (1999) 15824.

[25] A. F. Silva, I. Pepe, B. E. Sernelius, C. Persson, R. Ahuja, J. P. Souza, Y. Suzuki, Y. Yang, Electrical resistivity of accepter carbon in GaAs, J. Appl. Phys. 95 (5) (2004) 2532.

[26] A. F. Silva, J. Pernot, S. Contreras, B. E. Sernelius, C. Persson, J. Carmassel, Electrical resistivity and metal-nonmetal transition in n-type doped 4H-SiC, Phys. Rev. B 74 (2006) 245201.

[27] S. Chakravarty, G.-L. Ingold, S. Kivelson, A. Luther, Onset of global phase coherence in josephson-junction arrays: A dissipative phase transition, Phys. Rev. Lett. 56 (21) (1986) 2303.

[28] B. G. Orr, H. M. Jaeger, A. M. Goldman, Local superconductivity in ultrathin Sn films, Phys. Rev. B 32 (11) (1985) 7586(R).

[29] H. M. Jaeger, D. B. Haviland, B. G. Orr, A. M. Goldman, Onset of superconductivity in ultrathin granular metal films, Phys. Rev. B 40 (1) (1989) 182.

[30] D. B. Haviland, Y. Liu, B. Nease, A. M. Goldman, The onset of superconductivity un ultrathin amorphous metal films, Phisica B 165-166 (1990) 1457.

[31] S. Kobayashi, A. Nakamura, F. Komori, Critical sheet resistance for global superconductivity in granular aluminium films, J. Phys. Soc. Jpn. 59 (12) (1990) 4219.