The electrical resistivity of epitaxially deposited chromium films

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Abstract. We studied the electrical resistance and crystal structure of epitaxial chromium (Cr) films. The lattice constant of the Cr films is larger than that of the bulk Cr because the sample and the substrate MgO have different lattice constants. An chromium oxide layer having a thickness of 1 nm was found on all films from the result of X-ray reflectivity measurements. Although there is sample dependence in electric resistance of Cr films, it is remarkable that a zero resistance was observed for one film of 50 nm thick. \( T_C \) is obtained to be 3.2 K, which is about twice the previous reports. The large upper critical field is obtained to be \( H_{C2} = 13 \) kOe, and it suggests that Cr may belongs to a type II superconductor.

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 2 K[1, 2]. Such behavior is related to the structural phase transition under pressure from the ferromagnetic bcc (\( \alpha \)-Fe) phase to the paramagnetic hcp (\( \epsilon \)-Fe) phase[3].

Chromium (Cr), an antiferromagnet below the Neél temperature \( T_N = 311 \) K[4] 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[5, 6].

On the other hand, Schmidt et al. reported that thin films of Cr metal suppress the antiferromagnetic ordering and become superconductive at \( T_C \sim 1.5 \) K[7, 8]. From the point of view not only of pure research but also of applied and practical one, there are many examples of superconducting thin films. But almost all of them were those in which superconductivity disappears when the film thickness is made thin[9, 10]. It is likely to make a superconducting electron pair when it becomes thinner than the mean free path of electrons. Taking account that the bulk Cr does not show superconductivity, the relationship between film thickness and...
existence of superconductivity of Cr is opposite to the other examples of superconducting thin films.

Assuming that the magnetic correlation interaction is suppressed by controlling the film thickness, Cr may show a magnetic order-disorder transition tuned by the film thickness, and unconventional superconductivity may occur at the quantum critical point of $T_N \to 0$, where an electron pair appears due to quantum fluctuation. Such quantum phase transitions have been reported in strongly correlated electron systems, where various parameters such as pressure and magnetic field have been used by a driving force\[11, 12, 13, 14, 15, 16\].

However, quantum phase transition using the film thickness as a driving force has not been discovered in thin films at all. Generally, the three-dimensional electron system such as bulk compounds and two-dimensional one such as thin films are described by completely different Hamiltonian. That is, film thickness is an effective parameter that can directly control dimensionality, and it is interested in whether Cr is the first case of the new quantum phase transition tuned by film thickness.

It seems that there is still insufficient data for Cr films because neither the resistivity drop nor the Meissner effect has been reported yet\[7, 8\]. Recently we have studied the electrical resistance of polycrystalline Cr films, but it is difficult to conclude whether a superconducting transition occurs because of the large residual resistivity at low temperature\[17\]. In the present study, we prepare single crystal films of Cr, and perform precise electrical resistance measurements of Cr thin films in a wide temperature range and a magnetic field.

2. Experimental method

Single-crystal Cr films of 50 nm thick were fabricated epitaxially using a conventional magnetron sputtering device in ultrahigh vacuum below $2 \times 10^{-6}$ Pa. The Ar pressure during deposition was 0.1 Pa. The substrate for growing Cr epitaxially (001) is MgO. X-ray diffraction measurements were carried out using Rigaku MiniFlex II. The lattice constant $a$ is obtained to be between 2.974 and 2.976 Å which is larger than that of the bulk Cr, 2.880 Å\[18\]. It may come from the fact that the lattice constant of MgO, $a = 4.213$ Å is larger than $\sqrt{2}a = 4.073$ Å in bulk Cr. It suggests that the surface of the Cr layer can be subjected to the (110) orientation on the (001) MgO substrate. X-ray reflectance measurements were also carried out using the Rigaku SmartLab to estimate the film thickness, density, surface roughness, interface roughness, etc.

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. Result and discussion

3.1. X-ray reflectivity

Figure 1 shows the X-ray reflectivity profile of the epitaxial Cr film of 50 nm thick. Vibration appears in the reflected intensity due to the interference of the reflected light for each layer constituting the film. Figure 2 shows the fast Fourier transform (FFT) on this profile. If only the Cr film is present on the substrate, only one peak should appear at the position of 50 nm due to the interference between the Cr thin film and the substrate. However, in this result, two peaks were observed not only at around 50 nm but also at around 1 nm, which corresponds to the film thickness of the chromium oxide film such as CrO$_2$ generated by the oxidation of Cr on the surface. It means that an chromium oxide layer of 1 nm thick was formed on a Cr film of 50 nm thick.
Figure 1. X-ray reflectivity profile of Cr film of 50 nm thick.

Figure 2. Relative Fourier transform magnitude calculated from the result of Figure 1.

3.2. Electrical resistivity

Figure 3 shows the electrical resistivity $\rho(T)$ of several epitaxial Cr films of 50 nm thick as a function of temperature between 0.5 and 350 K. For Cr#1 and Cr#2 sample, $\rho$ is 14.0 and 16.6 $\mu\Omega$cm, respectively. Both $\rho(T)$ curves decrease with decreasing temperature and show a hump around 300 K. Such behavior compares with previous studies for epitaxial Cr films of 200 and 400 nm thick[17] and for the bulk one[19]. It is consistent with the fact that the bulk Cr is an itinerant antiferromagnet with $T_N$ below which the incommensurate spin density wave is stabilized[4, 5, 6]. Both for Cr#1 and Cr#2 sample, $T_N$ is obtained to be 288 K, where a minimum is observed in the temperature derivative of the resistivity $d\rho/dT$ as shown in the inset of Fig. 4. Note that $T_N$ is lower than that of the bulk Cr[5, 6].

Next, we focus the sample dependence observed in $\rho(T)$ curve. $\rho(T)$ curve for Cr#3 sample also decreases with decreasing temperature and shows a hump at around 300 K. But the magnitude of $\rho$ is much larger than that of Cr#1 and Cr#2 samples and of previous reports. $T_N$ is obtained to be 285 K for Cr#3 sample. The data of Cr#4 shows the result of Cr#3 sample after four wires are removed and re-bonded again. For Cr#4 sample, on the other hand, the magnitude of $\rho$ is the largest in that of all samples, and no anomaly due to any magnetic phase transition is observed in the $\rho(T)$ curve.

Figure 4 shows the electrical resistivity of epitaxial Cr films of 50 nm thick at low temperature. For Cr#1 and Cr#2 samples, $\rho(T)$ becomes almost constant below 5 K within the experimental error, indicating that superconducting transition does not occur. For Cr#3 sample, on the other hand, the resistance drops is observed as shown in the inset of Fig. 4. $T_C$ is obtained to be 1.36 K which is close to that of the previous reports[7, 8]. But it is difficult to conclude whether superconducting transition occurs in Cr#3 sample since the electrical resistivity is not zero. Moreover, the magnitude of the resistivity drop ratio 0.34 % is very small. Such small resistance drop is also observed in the previous study for polycrystalline films[17]. The following possibilities can be considered as factors causing such behavior. First, some chromium oxide
layer produced on a film surface is partially superconducting. Second, crystalline impurities in Cr may be superconducting or show some magnetic transition. Third, taking account that $T_C$ is enhanced in granular aluminum films[20], aluminum wires as electrodes may create grains on the surface of Cr film.

It is remarkable that zero resistivity is observed for Cr#4 sample, for which an anomaly in the $\rho(T)$ curve due to the antiferromagnetic transition is suppressed as shown in Fig. 3. Such behavior can not be explained by superconductivity of aluminum wires, and it is highly likely that Cr or its oxide shows superconductivity below $T_C$. The superconducting transition temperature is obtained to be $T_C = 3.2$ K, which is nearly the twice that of the previous
Taking account that Cr#3 and Cr#4 are same sample but the different results are shown in the electrical resistivity, it suggests that the sample is partially superconductivity in Cr#3 sample. Here, we attempted to measure the electrical resistivity at magnetic field as shown in Figure 5. $T_C$ shifted to the lower temperature side as the magnetic field is increased. Figure 6 shows the temperature and magnetic field phase diagram of superconductivity obtained from Fig. 5.

Extrapolated from the plotted data, the upper critical field at absolute zero was determined as $H_{C2} = 13$ kOe. Generally, most of the superconducting metal elements such as Al and Sn belongs to the type I superconductor, and their $H_{C2}$ is about several hundreds. However, taking account that $H_{C2}$ of Cr is one order of magnitude larger than that of the type II superconductor such as Nb ($H_{C2} = 1.980$ kOe) and V ($H_{C2} = 1.420$ kOe)[18], Cr#4 sample may also belongs to a type II superconductor.

4. Summary

We have fabricated epitaxial chromium (Cr) films of 50 nm thick using magnetron sputtering. The lattice constant of the Cr films is larger than that of the bulk Cr. Since it is well known that lattice constant is strongly correlated to physical parameters such as magnetic exchange interaction and electric conduction, it is necessary to study whether the similar behavior occurs when the lattice constant varies depending on the film thickness in the magnetic film. From the results of the X-ray reflectivity measurements, it was found that the Cr film used in this study also has an chromium oxide layer of about 1 nm thick. Therefore, the influence of the oxide layer of the surface of Cr films can not be ignored even in the previous reports in which it was not discussed until now.

Although there is sample dependence in electric resistance of Cr films, it is remarkable that a zero resistance was observed for one sample. The upper critical field $H_{C2}$ of this sample is one to two orders of magnitude larger than the other metal element superconductor. The measurement of Meissner effect is planed in future although it is difficult to detect a signal because the thin film has a small sample volume the magnetism of the substrate becomes a large background. Moreover, it is needed to clear the condition such as the film thickness, density, surface roughness, interface roughness and the lattice constant under which zero resistance appears.

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