Highest conductivity oxide SrMoO₃ grown by a floating-zone method under ultralow oxygen partial pressure

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Single crystals of a highly conductive oxide SrMoO₃ have been grown by a floating-zone method under an argon atmosphere with ultralow oxygen partial pressure \( p(O_2) \approx 10^{-25} \) atm. The obtained single crystals of SrMoO₃ reveal quite low resistivity at 300 K \( \rho(300\, K) = 5.1 \times 10^{-12} \, \Omega \cdot \text{cm} \), which is the lowest to date in the values of \( \rho(300\, K) \) for all oxides. Resistivity and specific heat data suggest that electrons in SrMoO₃ behave as the Fermi liquid (correlated electron), and that its low resistivity is due to the extremely small electron-phonon interaction in SrMoO₃.

Transition-metal oxides are expected to play an important role in the next-generation semiconductor industry as a so-called high-\( k \) insulating material. Interconnecting the high-\( k \) layer and other existing parts of electronics is a problem yet to be solved. The development of highly conductive oxide materials for electrodes and interconnects is supposed to facilitate the successful application of the high-\( k \) transition-metal oxides. Concerning metallic oxides which show low resistivity, there are several compounds, such as ReO₃, PdCoO₂, SrRuO₃, and (La, Sr)CoO₃. In particular, SrRuO₃ (Ref. 3) and (La, Sr)CoO₃ (Ref. 4) have attracted much attention as an electrode material for ferroelectric random access memory (FRAM). The high cost of Re and Pd hinders the application of ReO₃ and PdCoO₂. In developing conductive oxides, isotropic conductivity is preferable to anisotropic because the high conductivity can be expected in a polycrystalline form with random orientations of grains. Therefore, (pseudo) cubic metallic oxides, which show low resistivity and consist of low-cost elements, are in great demand from the application side.

According to the previous reports on SrMoO₃, this compound exhibits metallic conductivity. Wang et al. grew the polycrystalline thin-film samples of SrMoO₃ on SrTiO₃ substrates by pulsed laser deposition. The resistivity data of the samples reveal metallic behavior with \( \rho(300\, K) \approx 100 \, \mu \Omega \cdot \text{cm} \). Three-dimensional electrical conductivity is expected for SrMoO₃ because the crystal structure is a simple cubic perovskite. Among oxides, PdCoO₂ and ReO₃ exhibited the first and the second highest conductivity, respectively. However, the problem is the high material cost as mentioned above. Mo is preferred to Re and Pd in view of the raw material cost. These features make SrMoO₃ a candidate for oxide electrodes and/or interconnects material for large-scale integrated circuit (LSI) chips and FRAMs. A single crystal of SrMoO₃ is necessary for us to evaluate the intrinsic performance of SrMoO₃ as electric-conduction media. However, a single-crystal growth of SrMoO₃ has not been reported.

The difficulty in the single-crystal growth of SrMoO₃ lies in the fact that SrMoO₃ is stable only in a certain \( p(O_2) \) window, which depends on the temperature. For example, Kamata et al. showed that it is stable under an atmosphere with \( 10^{-12.5} \) atm \( \leq p(O_2) \leq 10^{-15} \) atm at 1200 °C. A usual way to realize such low \( p(O_2) \) is the use of H₂. However, H₂ gas always contains H₂O as an impurity, hence \( p(O_2) \) is determined according to the equilibrium \( H_2O \rightleftharpoons H_2 + 1/2 O_2 \), whose equilibrium constant depends on temperature. For a given \( H_2: H_2O \) ratio at room temperature, the final \( p(O_2) \) at an elevated temperature is a sole function of the temperature. Meanwhile, we have another equilibrium \( \text{SrMoO}_3 \rightleftharpoons 1/2 \text{O}_2 \rightleftharpoons \text{SrMoO}_4 \) in the system. Its equilibrium, \( p(O_2) \) is also dependent on temperature. In preparation of polycrystalline specimens, we can match \( p(O_2) \)'s of the two equilibriums by choosing the appropriate temperature. In contrast, we have to stick to a certain temperature in single-crystal growths since the temperature near the melting point of the target material has to be used. This is why we developed an oxygen-pump system, which can adjust \( p(O_2) \) in the furnace at any value between 0.2 and \( 10^{-31} \) atm. We can perform a single-crystal growth at the \( p(O_2) \) value that stabilizes the target oxide at the imposed temperature constraint.

In the single-crystal growth of SrMoO₃ by a floating-zone (FZ) method, polycrystalline SrMoO₃ was synthesized by a conventional solid-state reaction technique first. The equimolar mixture of powders of SrCO₃ and MoO₃ were ground and sintered at 1173 K in air for 12 h. We confirmed that the obtained sample consisted of a single phase of SrMoO₄ by x-ray diffraction. Second, the powder of SrMoO₄ was pressed into a rod, and was sintered at 1273 K in flowing...
FIG. 1. (Color) Single-crystalline SrMoO$_3$: (a) An obtained single crystal of SrMoO$_3$, and (b) a shaped single crystal of SrMoO$_3$ with two voltage probes (inner) and two current ones (outer) for resistivity measurement.

H$_2$ gas for 1 h. The powder x-ray diffraction pattern of the rod after this deoxidizing treatment indicated a single phase of SrMoO$_3$. The rod was then set in a FZ furnace (NEC Machinery, SC-II-MDH) equipped with a newly developed oxygen pump system. The oxygen pump using yttria-stabilized zirconia (YSZ) can lower the p(O$_2$) of Ar down to 10$^{-31}$ atm. The produced Ar gas flows into the FZ furnace. The exhaust gas from the FZ furnace returns to the oxygen pump system. The value of p(O$_2$) in the exhaust is measured by a YSZ oxygen sensor, which is equipped with the oxygen pump system (outside the furnace). The temperature of the sensor is kept at 973 K, at which the sensor works accurately. The p(O$_2$) in the furnace can be fixed at any point between 0.2 and 10$^{-31}$ atm by the proportional, integral and derivative (PID) feedback control. The growth of crystals was performed in Ar with p(O$_2$) = 10$^{-25}$ atm at the feeding speed of 1 mm/h. The crystal growth temperature was determined as ~2000 K with a radiation thermometer. We confirmed that the obtained sample was made of single crystals of SrMoO$_3$ by the Laue photograph. The typical size of the crystals was 0.5–1 mm. The obtained single crystal of SrMoO$_3$ is shown in Fig. 1(a). The cleaved surface corresponds to the (111) plane of SrMoO$_3$. Resistivity was measured by a standard four-probe method in the temperature range of 36 mK–300 K. The sample shaped into a rectangular parallelepiped was used for the resistivity measurement in order to obtain an exact value of resistivity, as shown in Fig. 1(b). The distance between the voltage electrodes was taken at the innermost edges of the silver-paste bumps, so that the calculated resistivity would be the higher bound. Specific heat was measured by the relaxation method (Quantum Design, PPMS) in the temperature range of 2–10 K.

Figure 2 shows the temperature dependence of resistivity for a single crystal of SrMoO$_3$. At all temperatures, it exhibited metallic behavior with a positive temperature derivative. No superconducting transition was observed down to 36 mK.

We note that the single crystal of SrMoO$_3$ reveals quite low resistivity of 5.1 $\mu$Ω cm at room temperature, which is the lowest in the values of $\rho$(300 K) among oxides. The residual resistivity ratio $\rho$(300 K)/$\rho$(3 K) is about 14. The inset in Fig. 2 shows the plot of $\rho$ versus $T^2$. Below $T^2=140$ K, the resistivity is well described with $\rho=\rho_0 + A/T^2$, which indicates that the temperature dependence of the resistivity is dominated by electron-electron scattering. Fitting with the above equation gives $\rho_0=0.35$ $\mu$Ω cm and $A=7.0 \times 10^{-5}$ $\mu$Ω cm/K$^2$.

The specific heat data for single-crystalline SrMoO$_3$ are plotted as $C/T$ versus $T^2$ in Fig. 3. The data follow a straight line below 10 K. Therefore, the data below 10 K are expressed by the sum of a linear term for the normal electronic contribution $\gamma T$ and the lattice contribution $\beta T^3$ as in the Debye model $C=\gamma T+\beta T^3$ ($\beta=12 \pi^4 N k_B/5 \theta_D^3$, where $\theta_D$ is the Debye temperature). The least-squares fitting to this equation below 10 K yields the electronic specific heat coefficient $\gamma=7.9$ mJ/mole K$^2$ and the Debye temperature $\theta_D=440$ K. The value of $\gamma$ of the single crystal is in agreement with that of the polycrystalline. The Kadowaki–Woods ratio of SrMoO$_3$ ($A/\gamma^2=1.1 \times 10^{-6}$ $\mu$Ω cm/(mJ/K mole)$^2$) is close to that of the heavy-fermion compounds ($A/\gamma^2=1.0$...
SrMoO$_3$ falls on this trend, we may safely conclude that its scattering at high temperature. Electron scattering at low temperature and electron-phonon dependence of electrical resistivity is dominated by electron-

Concerning layered oxide SrMoO$_3$ (this work) in which electrons behave like Fermi liquid. $T^*$ is defined as the temperature at which the resistivity data begins to deviate from the equation of $\rho=\rho_0+AT^2$. All data are based on single crystals. Concerning layered oxide (PdCoO$_2$, Sr$_2$RuO$_4$, Sr$_3$Ru$_2$O$_7$, and La$_{1.7}$Sr$_{0.3}$CuO$_4$), the value of in-plane resistivity at 300 K is used as $\rho(300 \text{ K})$. For PdCoO$_2$, the value of $\rho(270 \text{ K})$ is used instead of $\rho(300 \text{ K})$ because the resistivity data only below 270 K is reported. Meanwhile its value of $T^*$ is expected to be above 270 K because the data of the resistivity still obeys the equation $\rho=\rho_0+AT^2$ at 270 K (Ref. 2).

$10^{-5} \mu$\text{\Omega cm}/(mJ/K mol)$^2$. This suggests that electrons in SrMoO$_3$ behave as the Fermi liquid.

Here, we discuss why SrMoO$_3$ exhibits quite low resistivity $\rho(300 \text{ K})=5.1 \mu$\text{\Omega cm}. In Fermi-liquid metals, the $T$ dependence of electrical resistivity is dominated by electron-electron scattering at low temperature and electron-phonon scattering at high temperature. $T^*$ is interpreted as the temperature above which the electron-phonon scattering appreciably contributes to resistivity. Based on this idea, the smaller the electron-phonon interaction, the higher the value of $T^*$. On the other hand, the smaller $\rho(300 \text{ K})$ itself should be a result of the weaker electron scattering by phonons in a compound. The value of $\rho(300 \text{ K})$ is therefore expected to decrease with increasing $T^*$. Figure 4 shows the plot of $T^*$ versus $\rho(300 \text{ K})$ for a variety of transition-metal oxides in which electrons behave as the Fermi liquid.\footnote{10,11} This figure clearly justifies the above argument. Since the point for SrMoO$_3$ falls on this trend, we may safely conclude that its low resistivity is due to extremely small electron-phonon interaction in SrMoO$_3$. No observation of superconducting transition down to 36 mK may be consistent with this excessively small electron-phonon interaction.

In summary, single crystals of a highly conductive oxide SrMoO$_3$ have been grown by a FZ method under ultralow oxygen partial pressure $p(O_2)\sim 10^{-25}$ atm. The obtained single crystals reveal quite low resistivity at room temperature $\rho(300 \text{ K})=5.1 \mu$\text{\Omega cm}, which is the lowest to date in the values of $\rho(300 \text{ K})$ of all the oxides. From the results of resistivity and specific heat measurements, the Kadowaki–Woods ratio $\lambda/\gamma^2$ is estimated as $1.1 \times 10^{-6} \mu$\text{\Omega cm}/(mJ/K mol)$^2$, which implies that electrons in SrMoO$_3$ behave as the Fermi liquid. We find a clear correlation between $T^*$ and $\rho(300 \text{ K})$ for a variety of Fermi-liquid oxides, where $T^*$ is the temperature at which the resistivity data begins to deviate from the equation of $\rho=\rho_0+AT^2$. The data of $\rho(300 \text{ K})$ and $T^*$ for SrMoO$_3$ fall on this trend, which suggests that its low resistivity is due to the extremely small electron-phonon interaction in SrMoO$_3$.

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