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Synthesis of mid- to late-transition metal oxynitrides has attracted much attention as nontoxic inorganic pigments1–3 and visible-light active photocatalysts4–6 because they have good chemical stability and their band structure is suitable for visible light response. These early transition metal oxynitrides are widely synthesized by thermal ammonolysis, where precursor oxides are partially nitrided under high-temperature ammonia flow. In contrast, mid- to late-transition metal oxynitrides are partially nitrided under high-temperature ammonolysis: high-temperature ammonia reduces the main reactions—CoO is an antiferromagnetic insulator with rock salt (RS) structure (α = 4.263 Å),19 and CoN is a paramagnetic metal with ZB structure (α = 4.28 Å)20—varying the anion composition would induce structural, electrical, and/or magnetic phase transitions. Thus, in the present study, we synthesized epitaxial thin films of phase-pure AX-type CoONy with systematically controlled anion composition and investigated their crystal structures and physical properties.

In the last decade, early transition metal oxynitrides have attracted much attention as nontoxic inorganic pigments1–3 and visible-light active photocatalysts4–6 because they have good chemical stability and their band structure is suitable for visible light response. These early transition metal oxynitrides are widely synthesized by thermal ammonolysis, where precursor oxides are partially nitrided under high-temperature ammonia flow. In contrast, mid- to late-transition metal oxynitrides are partially nitrided under high-temperature ammonolysis: high-temperature ammonia reduces the main reactions—CoO is an antiferromagnetic insulator with rock salt (RS) structure (α = 4.263 Å),19 and CoN is a paramagnetic metal with ZB structure (α = 4.28 Å)20—varying the anion composition would induce structural, electrical, and/or magnetic phase transitions. Thus, in the present study, we synthesized epitaxial thin films of phase-pure AX-type CoONy with systematically controlled anion composition and investigated their crystal structures and physical properties.

CoONy thin films were fabricated on single-crystalline substrates of MgO (100) (α = 4.213 Å) and MgAl2O4 (MAO) (111) (α = 4.042 Å) by nitrogen-plasma-assisted pulsed laser deposition (NPA-PLD). The details of NPA-PLD are described elsewhere.21–23 In brief, a CoO pellet (99.9% purity), sintered at 1,200 °C for 1 h, was mounted with a nitrogen-plasma source. The substrate temperature (Tsub) during growth varied from 160 to 250 °C by an infrared lamp heater. The distance between the ablation target and the substrate was set at 50 mm. N2 gas activated by an excimer laser (λ = 248 nm, 0.66 J cm−2 pulse−1) was used as a nitrogen plasma source. The growth rate was 2 Å/s. The CoOxNy films were grown in a nitrogen plasma environment, and the as-grown films were examined by X-ray diffraction (XRD). The CoOxNy films were found to be single-phase, grown epitaxially on the MgO substrates. The crystallite size of the films was determined by the Scherrer equation using the full width at half maximum of the (002) diffraction peak. The crystallite size of the films was found to be about 20 nm. The electrical properties of the films were measured using a four-probe method in the temperature range of 4–300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2 Ω cm at 300 K. The electrical resistivity of the films was found to be very low, with a value of about 10−2
a radio-frequency (RF) plasma source (SVT Associates, model 4.5 in.) was introduced into the growth chamber as process gas. The input power of the RF plasma source was fixed at 200 W. The nitrogen content of each film was controlled by the partial pressure of nitrogen ($P_{N_2}$) and the deposition rate ($r$), which differed as a function of the pulse repetition rate of the excimer laser (1, 2, and 4 Hz). The deposition rate was determined from the deposition time and the film thickness evaluated by using a stylus profiler (Veeco, Dektak 6M). The thicknesses of the films were ∼50–105 nm.

The crystal structures of the obtained films were determined by X-ray diffraction (XRD) with a four-axis diffractometer (Bruker AXS, d8 discover) using Cu Kα radiation. The chemical compositions of the films were evaluated by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) (JEOL, JSM-7100F with JED-2300). The SEM-EDX results were calibrated to a sive X-ray spectroscopy (SEM-EDX) (JEOL, JSM-7100F with JED-2300). The SEM-EDX results were calibrated to a standard curve made from performing heavy ion elastic recoil detection analysis (ERDA) on several CoO$_x$N$_y$ thin films. ERDA measurements were performed with a 38.4 MeV $^{35}$Cl beam generated by a 5 MV tandem accelerator (Micro Analysis Laboratory, Tandem Accelerator, The University of Tokyo [MALT]). The recoils of nitrogen were identified by a ΔE–E telescope detector, comprising a gas ionization chamber and a Si solid-state detector. The experimental errors in $x$ and $y$ are about ±10%. The electrical resistivity was determined by using the four-probe method (Quantum Design, PPMS Model 6000) with Ag electrodes deposited by sputtering, of which ohmic contact was confirmed by current-voltage measurements. The magnetic properties were investigated by using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL), applying the magnetic field perpendicular to the film surface. The absence of ferromagnetic impurities, such as metallic Co or Co$_3$N, was confirmed by measuring the magneto-optical Kerr effect at room temperature.

To obtain epitaxial thin films of CoO$_x$N$_y$, the $T_s$ was first optimized at fixed $r$ (∼15 nm/h) and $P_{N_2}$ (1 × 10$^{-5}$ Torr). As shown in Fig. 1, CoO$_x$N$_y$ thin films with pseudocubic structure (RS or ZB, discussed later) grew epitaxially on both MgO (100) and MAO (111) at $T_s$ of 160–250 °C. However, at $T_s = 250$ °C, the sample on the MAO (111) substrate had a secondary phase of Co metal, which probably originated from thermal decomposition of CoO$_x$N$_y$, or (111)-oriented CoO$_x$N$_y$. In addition, the peak intensity weakened at higher temperatures on the MgO (100) substrate (Fig. 1(a), inset). Thus, in further experiments, we grew CoO$_x$N$_y$ thin films on MgO (100) at $T_s = 160$ °C.

Figure 2(a) plots the nitrogen contents $y/(x+y)$ of the CoO$_x$N$_y$ thin films as functions of $r$ and $P_{N_2}$. With increasing $r$, i.e., with increasing the relative supply rate of Co and O under the same $P_{N_2}$, the nitrogen content monotonically deceased, whereas it increased with increasing $P_{N_2}$. By tuning these two parameters, the anion composition of the CoO$_x$N$_y$ thin film could be controlled within the range of 0 ≤ $y/(x+y) ≤ 0.63$. While the O/Co ratio $x$ systematically decreased with increase of nitrogen amount $y/(x+y)$, the (N + O)/Co ratio $x+y$ were almost constant at unity (Fig. 2(b)), indicating the formation of AX-type compounds.

Next, we discuss the crystal structures of the CoO$_x$N$_y$ thin films in detail. The $θ$–20 XRD patterns (Fig. 3) and φ scans (see supplementary Fig. S124) of the films with various nitrogen contents revealed that all the films grew epitaxially on the substrate in a cube-on-cube manner without forming any impurity phases. The absence of Pendellosung fringe (Fig. 3(b)) is plausibly due to surface roughness of the films (several nanometers). As possible crystal structures with a pseudocubic cell, we considered $A_3X_4$-type spinel as well as AX-type RS and ZB structures. Among these three candidates, we excluded $A_3X_4$-type spinel from the asymmetric scan of $hhh$ diffraction because none of the films showed the 111 diffraction characteristic of the spinel structure ($2θ ≈ 18°$). This result was consistent with the composition analysis (Fig. 2(b)). The intensity ratio of 111 to 002

![FIG. 1. $θ$–20 XRD patterns of CoO$_x$N$_y$ thin films grown at various $T_s$, on (a) MgO (100) and (b) MAO (111) substrates. The inset in (a) shows magnified plots near the 002 diffraction peaks. The asterisk in (b) indicates the diffraction peak of Co (111) or RS-CoO$_x$N$_y$ (002) from secondary phase.](image-url)

![FIG. 2. (a) Nitrogen contents $y/(x+y)$ of the CoO$_x$N$_y$ thin films grown on MgO (100) with varying deposition rate and nitrogen partial pressure. (b) Detailed chemical composition of the CoO$_x$N$_y$ thin films as a function of $y/(x+y)$.](image-url)
diffraction $I_{111}/I_{002}$ is a good way to distinguish RS and ZB structures: $I_{111}/I_{002}$ is $\sim 0.5$ for RS CoO$_{2+y}$ and $\sim 3$ for ZB CoN.\cite{25} Figure 4 summarizes the in-plane ($a$ axis) and out-of-plane ($c$ axis) lattice constants, unit cell volumes, and $I_{111}/I_{002}$ values of the CoO$_N$ thin films. The $I_{111}/I_{002}$ values and in-plane lattice constants were evaluated from 002 and 111 diffraction of the same film grown on MgO (100) substrate. All these structural parameters abruptly increased at $y(x+y) \sim 0.5$. The $I_{111}/I_{002}$ values at $y(x+y) \leq 0.43$ and $y(x+y) > 0.51$—0.6–1.2 and 3.7–6.1, respectively—are consistent with those expected for RS and ZB. Furthermore, the increase in unit cell volume at $y(x+y) = \sim 0.5$, $\sim 10\%$, is equivalent to that predicted by the first-principles calculation of CoN with RS and ZB structures, $\sim 25\%$.\cite{27} These results indicate that the structural phase transition from RS to ZB occurred at $y(x+y) \sim 0.5$. We note that all of the films showed tetragonal distortion ($c > a$) due to compressive strain from the substrate. While the lattice constants slightly depended on film thickness due to partial relaxation from the substrate ($a > a_{\text{single}}$), the influence of film thickness on the lattice constant was small for the samples thicker than 50 nm (see supplementary Fig. S2).\cite{24}

The structural phase transition at $y(x+y) \sim 0.5$ might have been caused by a change in the average electronegativity of the anions. According to the Mooser–Pearson plot,\cite{28} the coordination numbers of materials tend to decrease with a decrease of average principal quantum number $n$ or electronegativity difference between cations and anions, $\Delta \chi$. For CoO$_N$, while $n = 3$ is constant, $\Delta \chi$ decreases from $\sim 1.8$ (CoO) to $\sim 1.3$ (CoN)\cite{29} as the nitrogen content $y$ increases from 0 to 1, which would induce the phase transition from RS (6 coordination) to ZB (4 coordination).

We also studied the electrical transport properties of the RS- and ZB-CoO$_N$ thin films with various anion compositions. Figure 5(a) shows the electrical resistivity $\rho$ of the CoO$_N$ thin films at room temperature. With increasing nitrogen content, the $\rho$ of the RS-CoO$_N$ thin films ($y/(x+y) \leq 0.43$) monotonically decreased from the order of $10^3 \Omega \cdot \text{cm}$ to $10^{3} \Omega \cdot \text{cm}$. This tendency is rationalized by considering hole doping into $p$-type CoO through nitrogen substitution for oxygen, although the high resistivity of the samples prevented verification of carrier type by Hall measurement. Notably, $\rho$ abruptly decreased between $y/(x+y) = 0.32$ and 0.34. At the same time, the $\rho$–$T$ curves of these films (inset of Fig. 5(a)) changed drastically: the insulating $\frac{d\rho}{dT}$ (on the order of $d\rho/dT \sim 10^{-2} \text{K}^{-1}$ at $y(x+y) = 0.32$) changed to $d\rho/dT \sim 0.34$ at $y(x+y) = 0.34$. The $d\rho/dT$ value finally became positive (i.e., metallic) at $y(x+y) = 0.43$ (T > 50 K). These changes strongly suggest that CoO$_N$ underwent an insulator-to-metal transition (IMT) at $y(x+y) = \sim 0.34$. We stress that a low $\rho$ on the $10^{-3} \Omega \cdot \text{cm}$ order together with composition-induced IMT has not yet been reported in CoO$_{2+y}$/Co$_{3+y}$ mixed valence cobalt oxides with octahedral coordination such as Co$_3$O$_4$\cite{17} Li-doped CoO (Li$_{x}$Co$_{1-y}$O)\cite{15,16} or La$_{1-x}$Sr$_{1+y}$CoO$_4$\cite{18}.

The $\rho$ values of the ZB-CoO$_N$ ($y/(x+y) \geq 0.51$) films are on the same order as that of polycrystalline ZB-CoO$_{0.5}$N$_{0.5}$ thin film containing an amorphous impurity phase, $\rho \sim 10^{-3} \Omega \cdot \text{cm}$,\cite{14} confirming that such a low $\rho$ is...
3.6 high-spin (HS) state, Co$_3$N$_4$ field. Among these possible Co$_3$N$_4$ spin (IS), or low-spin (LS) state depending on the crystal coordination, their electrical transport strongly depends of the insulator-to-metal transition. (b) Saturation magnetization ($M_S$) of the RS-CoO$_N$$_y$ thin films increased as the nitrogen content $y/(x+y)$ increased from 0 to 0.32. The small hysteresis ($H_{	ext{c}}\sim100$ Oe) in the $M$–$H$ curves may suggest weak ferromagnetism in these films. This systematic increase in $M_S$ values ($\leq0.14$ $\mu$B/Co) might be attributable to an increase in spin-canting angle induced by introduction of Co$^{3+}$, although the detailed mechanism remains unclear. However, further increasing the nitrogen content ($y/(x+y)\geq0.34$) caused $M_s$ to drop suddenly. We speculate that a magnetic phase transition occurred during the IMT of RS-CoO$_N$$_y$. An interesting feature is that the phase transition occurred at $y/(x+y)\approx1/3$, corresponding to local coordination geometry in which two of six anion sites of Co$_N$ octahedra are occupied by nitrogen. This suggests that the phase transition was caused by a special coordination structure, such that apical oxygen were fully substituted with nitrogen. Unfortunately, it was difficult to determine whether the metallic RS-CoO$_N$$_y$ and ZB-CoO$_N$$_y$ phases were paramagnetic or antiferromagnetic because precise interpretations of the $M$–$T$ curves were strongly hindered by the magnetic impurities in the MgO substrate. Spectroscopic techniques such as X-ray absorption near edge structure and X-ray magnetic circular dichroism might give further information on the coordination structure, magnetic properties, and spin state of CoO$_N$$_y$.

In summary, we synthesized CoO$_N$$_y$ epitaxial thin films ($0\leq y/(x+y)\leq0.63$) on MgO (100) single-crystalline substrates by using NPA-PLD. The obtained CoO$_N$$_y$ thin films showed a structural phase transition from RS to ZB as $y/(x+y)$ increased to $\sim0.5$. The room-temperature electrical resistivity of the CoO$_N$$_y$ films varied widely from $10^2$ $\Omega$cm to $10^4$ $\Omega$cm with nitrogen content. Notably, IMT appeared at $y/(x+y)\sim0.34$ in the RS-CoO$_N$$_y$ phase, whereas the RS-CoO$_N$$_y$ phase with higher nitrogen content showed a low resistivity in the order of $10^{-3}$ $\Omega$cm, possibly caused by the high electron-transfer rate between HS Co$^{3+}$ and IS Co$^{3+}$. An abrupt decrease in saturation magnetization suggests that a magnetic phase transition occurred simultaneously with the IMT, though further investigation is needed to understand the detailed magnetic properties of CoO$_N$$_y$. These results demonstrate that low-temperature epitaxial growth is a promising synthesis route for mid- to late-transition metal oxynitrides, which paves the way for exploring novel electronic functionalities in oxynitrides.

Finally, we briefly discuss the magnetic properties of the CoO$_N$$_y$ thin films. Figure 5(b) summarizes the $M$–$H$ curves and saturation magnetization ($M_S$) of the CoO$_N$$_y$ films at 100 K. Because CoO is an antiferromagnetic Mott insulator, hole doping through nitrogen substitution would affect its magnetic properties. Indeed, the $M_s$ of the RS-CoO$_N$$_y$ films increased as the nitrogen content $y/(x+y)$ increased from 0 to 0.32. The small hysteresis ($H_{	ext{c}}\sim100$ Oe) in the $M$–$H$ curves may suggest weak ferromagnetism in these films. This systematic increase in $M_S$ values ($\leq0.14$ $\mu$B/Co) might be attributable to an increase in spin-canting angle induced by introduction of Co$^{3+}$, although the detailed mechanism remains unclear. However, further increasing the nitrogen content ($y/(x+y)\geq0.34$) caused $M_s$ to drop suddenly. We speculate that a magnetic phase transition occurred during the IMT of RS-CoO$_N$$_y$. An interesting feature is that the phase transition occurred at $y/(x+y)\approx1/3$, corresponding to local coordination geometry in which two of six anion sites of Co$_N$ octahedra are occupied by nitrogen. This suggests that the phase transition was caused by a special coordination structure, such that apical oxygen were fully substituted with nitrogen. Unfortunately, it was difficult to determine whether the metallic RS-CoO$_N$$_y$ and ZB-CoO$_N$$_y$ phases were paramagnetic or antiferromagnetic because precise interpretations of the $M$–$T$ curves were strongly hindered by the magnetic impurities in the MgO substrate. Spectroscopic techniques such as X-ray absorption near edge structure and X-ray magnetic circular dichroism might give further information on the coordination structure, magnetic properties, and spin state of CoO$_N$$_y$. In summary, we synthesized CoO$_N$$_y$ epitaxial thin films ($0\leq y/(x+y)\leq0.63$) on MgO (100) single-crystalline substrates by using NPA-PLD. The obtained CoO$_N$$_y$ thin films showed a structural phase transition from RS to ZB as $y/(x+y)$ increased to $\sim0.5$. The room-temperature electrical resistivity of the CoO$_N$$_y$ films varied widely from $10^2$ $\Omega$cm to $10^4$ $\Omega$cm with nitrogen content. Notably, IMT appeared at $y/(x+y)\sim0.34$ in the RS-CoO$_N$$_y$ phase, whereas the RS-CoO$_N$$_y$ phase with higher nitrogen content showed a low resistivity in the order of $10^{-3}$ $\Omega$cm, possibly caused by the high electron-transfer rate between HS Co$^{3+}$ and IS Co$^{3+}$. An abrupt decrease in saturation magnetization suggests that a magnetic phase transition occurred simultaneously with the IMT, though further investigation is needed to understand the detailed magnetic properties of CoO$_N$$_y$. These results demonstrate that low-temperature epitaxial growth is a promising synthesis route for mid- to late-transition metal oxynitrides, which paves the way for exploring novel electronic functionalities in oxynitrides.

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“Nanotechnology Platform” (Project No. 12024046) of MEXT, Japan.

24See supplementary material at http://dx.doi.org/10.1063/1.4937431: In supplementary Fig. S1 we show phi scan plots of the CoO/Ci9N/Ci9 thin films. In Fig. S2 we indicate thickness dependence of the lattice constants of the CoO/Ci9N/Ci9 thin film.