



Cite this: *J. Mater. Chem. C*, 2015, **3**, 4438

Self-assembled *c*-axis oriented antiperovskite soft-magnetic CuNCo_3 thin films by chemical solution deposition†

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Preparation of antiperovskite thin films is challenging work due to their complex phase diagram and easy decomposition during processing, which hinder the fundamental studies and applications. Herein, we report the preparation of antiperovskite CuNCo_3 (CNC) thin films on several different single crystal substrates by chemical solution deposition. The results show that the derived CNC thin films are *c*-axis oriented regardless of the substrate orientation, suggesting the self-assembled *c*-axis orientation. The microstructures as well as the physical properties are investigated, showing that the CNC thin films are metallic and can be considered as a new type of soft-magnet with a ferromagnetic Curie temperature higher than 650 K. The results will provide an effective route for fabricating antiperovskite cobalt-based thin films as well as provide a prototype for the investigation of the growth mechanisms of complex metal nitride thin films by solution methods.

Received 5th February 2015,
Accepted 23rd March 2015

DOI: 10.1039/c5tc00349k

www.rsc.org/MaterialsC

1 Introduction

Transition-metal nitrides and carbides have unique physical properties, including thermal, catalytic activity, unusual magnetic properties, and high hardness and mechanical strength.^{1,2} As one typical type of transition-metal nitride and carbide, antiperovskite structured materials have been studied intensively due to their rich physical properties as well as potential applications. Antiperovskite metal nitrides and carbides AXM_3 ($A = \text{Mg, Cu, Ga, Al, Rh, etc.}$; $X = \text{N, C}$; $M = \text{Mn, Fe, Ni, Co, etc.}$) have been studied intensively both by experimental and theoretical methods. Novel properties including superconductivity in MgCn_3 and CuNNi_3 ,^{3,4} strong electron–electron correlation in AlCn_3 and GaCn_3 ,^{5,6} excellent magnetism in RhNFe_3 ,⁷ magnetostriction in CuNMn_3 ,⁸ giant negative thermal expansion in $\text{Cu}_{1-x}\text{Ge}_x\text{NMn}_3$ ⁹ and a near zero temperature coefficient of resistivity in $\text{Ag}_{1-x}\text{Cu}_x\text{NMn}_3$ ¹⁰ have been widely investigated.

To investigate the intrinsic physical properties of antiperovskites, it is desirable to obtain high-quality single crystals or thin films. However, it is a challenge to prepare antiperovskite

single crystals due to their high melting point and easy decomposition and complex phase diagram. On the other hand, various methods have been tried to deposit antiperovskite thin films including molecular beam epitaxy,¹¹ magnetron sputtering^{12,13} and so on. Although the Fe, Ni, and Mn-based antiperovskites have been widely investigated,^{14–16} the Co-based antiperovskite nitrides have not yet been studied intensively because of the experimental difficulty in growing high-quality single crystals or thin films of Co_4N . Matsuoka *et al.* prepared Co_xN films by reactive sputtering using the Co target with varying $\text{N}_2/(\text{N}_2 + \text{Ar})$ ratios and found that the main phases are Co, Co_2N and Co_3N .¹⁷ Oda *et al.* reported the successful growth of Co_4N thin films by reactive sputtering for the first time, and it was observed that the cubic lattice constant is 3.586 Å (with a Co/N composition ratio around 5.47), indicating high N vacancies in the derived thin films.¹⁸ Recently, by employing NH_3 plasma, Ito *et al.* reported the growth of $\text{Co}_x\text{Fe}_{4-x}\text{N}$ ($x = 0, 3, 4$) thin films on SrTiO_3 substrates by the molecular beam epitaxy method and the orbital and spin magnetic moments were characterized using X-ray magnetic circular dichroism (XMCD) measurements.¹⁹

To further investigate the properties as well as potential applications of antiperovskite based materials, it is desirable to develop an effective route for synthesizing high-quality antiperovskite thin films. Chemical solution deposition (CSD) is an effective route for fabricating thin films with the advantages of low-cost, easy set-up, and coating of large areas, which has been widely used in the past few years.^{20,21} Recently, we have reported on the successful preparation of epitaxial antiperovskite CuNNi_3

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5tc00349k

thin films by CSD for the first time.⁴ However, compared with CuNNi₃ the Co-based antiperovskites are more difficult to obtain phase-pure thin films due to the more complex phase diagram of Co–N including β -Co(N) (fcc), Co₄N (antiperovskite), Co₃N (hcp), Co₂N (orthorhombic) to CoN (NaCl/ZnS type) and so on.

Herein, we report the preparation of antiperovskite CuNCo₃ (CNC) thin films by chemical solution deposition on different single crystal substrates for the first time. The derived CNC thin films show a cubic lattice constant about 3.75 Å, which is similar to that of the theoretical result ($a = 3.74$ Å) for the antiperovskite structure Co₄N,²² indicating the near stoichiometry of nitrogen. The results show that the thus-derived CNC thin films are *c*-axis oriented irrespective of the substrate orientation, indicating the self-assembled *c*-axis orientation. The relationship between processing, microstructures, and magnetic and electronic transport properties has been discussed, and the results show that CuNCo₃ can be considered as a new type of soft magnet with a Curie temperature above room temperature. The results will provide an effective route for depositing high-quality Co-based antiperovskite thin films as well as provide a useful prototype for the investigation of the growth mechanisms of complex antiperovskite thin films by solution methods.

2 Experimental

CNC thin films were prepared by CSD. Cupric nitrate (Cu(NO₃)₂·3H₂O) and cobalt acetate (Co(CH₃COO)₂·4H₂O) (in the molar ratio of 1:3) were dissolved into 2-methoxyethanol and glacial acetate acid (in the volume of 1:1) at 80 °C, and stirred at this temperature for 20 minutes, and then stirred at room temperature for more than 6 hours. The used solution was adjusted to a concentration of 0.1 mol L^{−1}. Before the deposition process, all the substrates were ultrasonically cleaned with acetone, ethyl alcohol and deionised water subsequently, and then cleaned in a plasma-cleaner for 10 minutes. All the thin films were fabricated by the spin-coating method with a rotation speed of 5000 rpm and a time of 10 s, then baked in air at 150 °C for 2 minutes and pyrolyzed in air at 350 °C for 10 minutes. In order to enhance the thickness, the above process was repeated for 12 times. Finally, the thin films were annealed at 800 °C for 2 hours under a flowing ammonia atmosphere with 1 atm pressure. Here, the CuNCo₃ thin films deposited on (001)- and (111)-oriented LaAlO₃ (LAO) single-crystal substrates, and YSZ(001) and Si(001) single-crystal substrates are denoted as CNC/LAO(001), CNC/LAO(111), CNC/YSZ(001) and CNC/Si(001), respectively.

The crystal phase and quality were analysed by X-ray diffraction with a monochromatic Cu-K_α radiation on a Philips X'pert Pro machine (XRD, Nickel filter and Bragg–Brentano geometry, PANalytical B. V., Almelo, Netherlands). The surface morphology was determined using a field-emission scanning electronic microscope (FE-SEM, FEI-designed Sirion 200, Hillsboro, OR). The film thickness and the interface were checked using a transmission electron microscope (TEM, JEM-2010, JEOL Ltd., Japan). The chemical states of Cu, Co and N were analysed using an X-ray photoelectron spectrometer (XPS, ESCALAB250, Thermo, USA).

The magnetization measurements were performed on a Quantum Design superconducting quantum interface device (SQUID). Electrical transport properties were investigated on a physical property measurement system (PPMS, Quantum-designed) using the standard four-point probe technique.

3 Results and discussion

Fig. 1 shows the XRD θ – 2θ patterns for all derived CNC thin films on different substrates. It is seen that only CNC(002) and (004) diffraction peaks can be clearly observed except for the diffraction peaks from the substrates, and there exist no undesirable phases such as Cu and Co, CoN, Co₂N, Co₃N, Cu–N, Cu–O and Co–O and so on. It is seen that there exist very weak odd diffraction peaks such as the (00 l) peak. The very weak odd diffraction peaks in CNC thin films can be attributed to the structure scattering as well as the atomic scattering factor due to the smaller atomic number of the Cu atom ($Z = 29$) as compared to other antiperovskite materials such as the In-based antiperovskite materials ($Z = 49$), which has been confirmed by previous reports on Cu- and In-based antiperovskite materials.^{4,23–27} In addition, the extinction or very weak peak intensity of the odd diffraction peaks has been also verified in the Fe, Co, and Mn-based antiperovskite thin films.^{11,28,29} The result suggests that chemical solution deposition is effective in growing phase-pure CNC thin films although this material is a type of ternary nitride, which is very difficult in growing phase-pure thin films. Moreover, it is interesting to observe that all derived thin films show *c*-axis orientation regardless of the orientation of the substrates even though the substrate is the Si(001) substrate with a parasitic SiO₂ layer that can be considered as an amorphous substrate, indicating the self-assembled *c*-axis orientation.

In order to determine the out-of-plane orientation as well as the in-plane orientation, the measurements including the rocking curves and in-plane ϕ -scanning are carried out. The obtained results of rocking curves are shown in the corresponding insets of Fig. 1 and there exists no in-plane orientation for all derived thin films. The full width at half-maximum (FWHM) in rocking

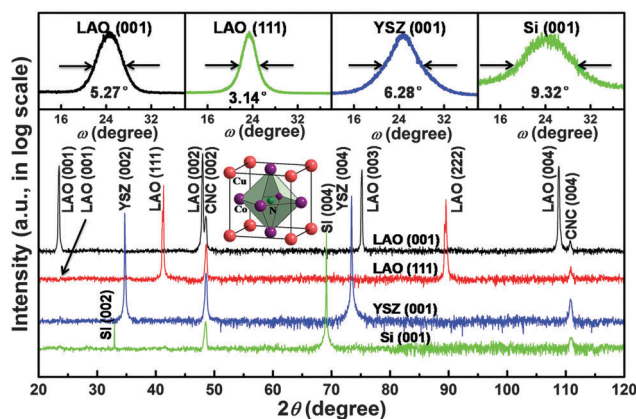


Fig. 1 XRD patterns of the derived CNC thin films. Rocking curves are displayed in the top insets. The cubic structure of CNC is shown as the middle inset.

curves is 5.27, 3.14, 6.28 and 9.32° for the CNC thin films on LAO(001), LAO(111), YSZ(001) and Si(001), respectively.

To obtain highly oriented thin films, the thin film should be processed so that the heterogeneous nucleation occurs at the interface between the thin film and the substrate. It is recognized that the small lattice mismatch is beneficial for heterogeneous nucleation resulting in highly oriented thin films. However, the derived CNC thin films show *c*-axis orientation although the lattice mismatch is different for CNC on LAO and YSZ, and the lattice of the LAO(111) substrate is anisotropic and the substrate SiO₂/Si can be considered as an amorphous substrate, which suggest that the lattice match does not play the dominant role in the determination of the CNC orientation. In fact, for the case where only nucleation at the substrate interface occurs, crystallographic growth along the fast growth direction can also result in highly oriented films. That means the grains with the lowest surface energy will nucleate first when the precursor phase is transferred to the crystallized phase at the substrate in chemical solution deposition processing,³⁰ resulting in highly oriented thin films. Although there has been no relative report on the surface energy of CNC, it is reasonable to conjecture that the (001) surface has the lowest surface energy in CNC, resulting in the self-assembled *c*-axis orientation.

The lattice constant *a* for all derived CNC thin films is calculated by the Bragg formula using the CNC(004) diffraction peaks. The lattice constant *a* is calculated to be 3.7475, 3.7429, 3.7442 and 3.7497 Å for the CNC thin films on LAO(001), LAO(111), YSZ(001) and Si(001), respectively. The variation in the lattice constant can be attributed to different nitrogen contents in the derived thin films as discussed below. Moreover, the lattice constant is larger than that of the previous experimental result (*a* = 3.52 Å)²⁸ and similar to that of the theoretical result (*a* = 3.74 Å)²² for Co₄N. The lattice constant is also calculated by first-principles density functional theory (DFT) using the projected augmented-wave (PAW) method with the generalized gradient approximation (GGA) as implemented in the ABINIT code. It is found that the lattice constant is decreased with decreasing N content and the lattice constant of the stoichiometric CNC is calculated to be 3.766 Å, which is in very good agreement with the experimental result (*a* = 3.75 Å) indicating the near stoichiometry of the derived CNC thin film. Previously, it is calculated that the lattice constant of Co₄N is decreased with nitrogen vacancies,²² and therefore the decreased lattice constant in experimental Co₄N thin films can be attributed to the nitrogen vacancies. As discussed above, it is suggested that Cu doping is beneficial for nitrogen incorporation into the lattices, which can be explained from the atomic electro-negativity. It is recognized that the larger difference between the electro-negativity of atoms can lead to the affinity of weaker atoms, and *vice versa*. By comparing the electro-negativity difference between Co, Cu and N, it can be drawn that the affinity between Co and N is weaker than that between Cu and N.³¹ Therefore, Cu atoms will be combined with more nitrogen atoms as compared with Co atoms, resulting in the enhanced nitrogen content in CNC as compared with that of Co₄N.

In order to clarify the reaction mechanisms, the XRD measurements are carried out for the thin films deposited on the Si(001) substrates. The obtained results are shown in Fig. 2. After pyrolysis in air, cupric nitrate and cobalt acetate are decomposed into

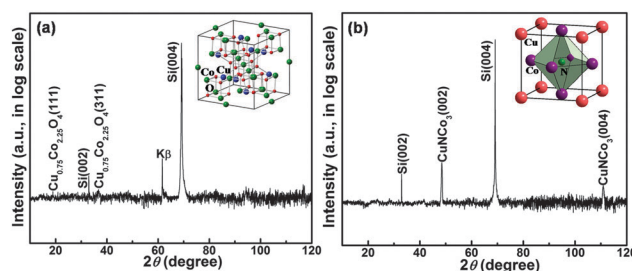
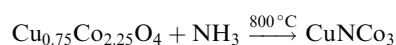
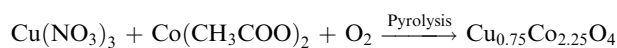


Fig. 2 XRD patterns of (a) the pyrolyzed thin film and (b) the crystallized thin film under a NH₃ atmosphere deposited on the Si(001) substrate. The cubic structure of Cu_{0.75}Co_{2.25}O₄ and CuNC₃ are shown in the corresponding inset.

Cu_{0.75}Co_{2.25}O₄ (cubic, PDF Card no. 01-078-2176).^{32,33} The metal nitrate CuNC₃ is formed when Cu_{0.75}Co_{2.25}O₄ is heat-treated under flowing NH₃ gas. The detailed processes are shown as follows.



It is noted here that the crystallization of the pyrolyzed Cu_{0.75}Co_{2.25}O₄ thin film will be enhanced after annealing at 800 °C for 2 h under air. However, if the Cu_{0.75}Co_{2.25}O₄ thin film is annealed at 800 °C for 2 h under the forming gas (20% H₂ and 80% N₂) metallic Cu and Co will appear without the CuNC₃ phase. Then, the thin film composed of metallic Cu and Co will be formed into CuCo₂N_{0.6}³⁴ with residual Co after annealing at 800 °C for 2 h under a flowing NH₃ atmosphere, which indicate that nitrogen is more difficult to be incorporated into the cubic metal lattices. The details of the chemical reactions can be seen in the ESI.†

Fig. 3(a) and (b) show the surface FE-SEM results for CNC thin films on different LAO substrates. It is seen that the two thin films are relatively smooth and dense. Furthermore, it is

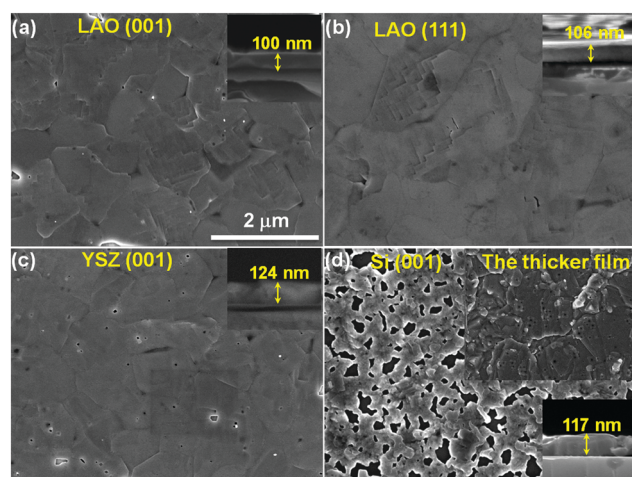


Fig. 3 FE-SEM results for all CNC thin films on different substrates: (a) LAO(001), (b) LAO(111), (c) YSZ(001) and (d) Si(001), and the inset shows the thicker CNC/Si(001) film. The thickness information is shown in the corresponding insets of Fig. 3.

seen that clear grain boundaries are observed for the CNC/LAO(001) thin film, and the boundaries are obviously depressed for the CNC/LAO(111) thin film, which can be attributed to the different nitrogen contents in derived CNC thin films confirmed by XPS measurements as discussed below. Fig. 3(c) and (d) show the FE-SEM results of the CNC/YSZ(001) thin film and the CNC/Si(001) thin film, respectively. It is seen that the CNC/YSZ(001) thin film is also relatively smooth and dense, while the CNC/Si(001) thin film shows the characteristic of dewetting. The dewetting can be attributed to the large difference in the thermal expansion coefficient between the CNC thin film and the Si substrate.³⁰ As reported previously³⁵ dewetting can be decreased as the thin film thickness increases as shown in the inset of Fig. 3(d), which gives a continuous and dense CNC/Si(001) thin film morphology. The thickness measured using a cross-sectional FE-SEM is determined to be 100, 106, 124, 117 nm for the CNC thin films on LAO(001), LAO(111), YSZ(001) and Si(001), respectively, as shown in the insets of Fig. 3.

Fig. 4(a) shows a typical cross-sectional HRTEM result for the CNC/LAO(001) thin film. The selected area electron diffraction (SAED) patterns from the $[110]$ beam direction is presented in Fig. 4(b). It is seen that the thickness is about 100 nm for the derived thin film as shown in the inset of Fig. 4(a), which is consistent with the cross-sectional FE-SEM measurement. Additionally, the lattice constant is determined to be 3.74 Å from both the c -axis strips and the SAED pattern, which is in agreement with the result from the XRD measurement. Fig. 4(c) shows the cross-sectional HRTEM result for the CNC/Si(001) thin film. The selected area electron diffraction (SAED) pattern from the $[100]$ beam direction is presented in Fig. 4(d). It is seen that the intensity of the odd diffraction pots are weaker than that of the even diffraction pots, which is the same as the XRD results. From the inset of Fig. 4(c), an amorphous SiO_2 layer between the film and the substrate can be clearly seen. Additionally the derived thin film is 117 nm in thickness.

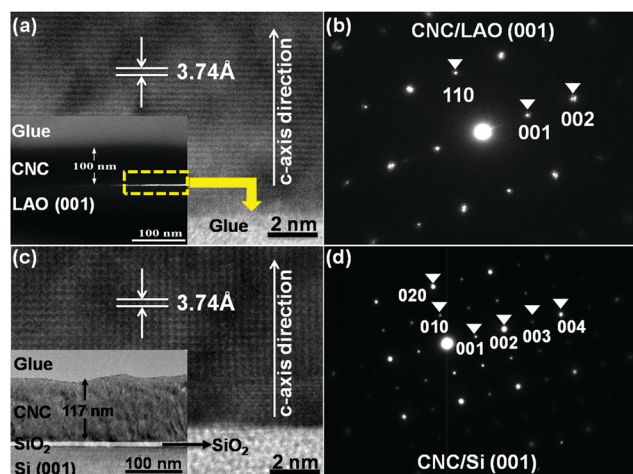


Fig. 4 (a) The cross-sectional HRTEM result of the CNC/LAO(001) thin film and the inset shows the film thickness. (b) The corresponding SAED pattern from the $[110]$ beam direction. (c) The cross-sectional HRTEM result of the CNC/Si(001) thin film and the inset shows the film thickness. (d) The corresponding SAED pattern from the $[100]$ beam direction.

The thin film CNC/LAO(001), although, tends to exfoliate from the substrate, the orientation of the exfoliated thin film inherits the morphology near the interface between the film and the substrate. For the thin film CNC/ SiO_2 /Si, the substrate SiO_2 /Si can be considered as an amorphous substrate, and the film still exhibits c -axis orientation. Moreover, c -axis strips parallel to the interface can be clearly seen, which further confirms the c -axis self-orientation in the derived CNC thin films. The observation of c -axis strips parallel to the interface suggests that the c -axis self-orientation affords the heterogeneous nucleation at the interface as discussed above.

XPS spectra for Cu 2p, Co 2p and N 1s of four typical CNC thin films are shown in Fig. 5(a)–(c), respectively. The Cu $2p_{3/2}$ main peaks have a satellite structure on the higher binding energy (BE) side, indicating the covalency of Cu 3d–N 2p hybridization as discussed in previous reports on $\text{Mn}_{3.6}\text{Cu}_{0.4}\text{N}$.¹⁶ The Co $2p_{3/2}$ orbital binding energy band can be fitted roughly by two peaks,

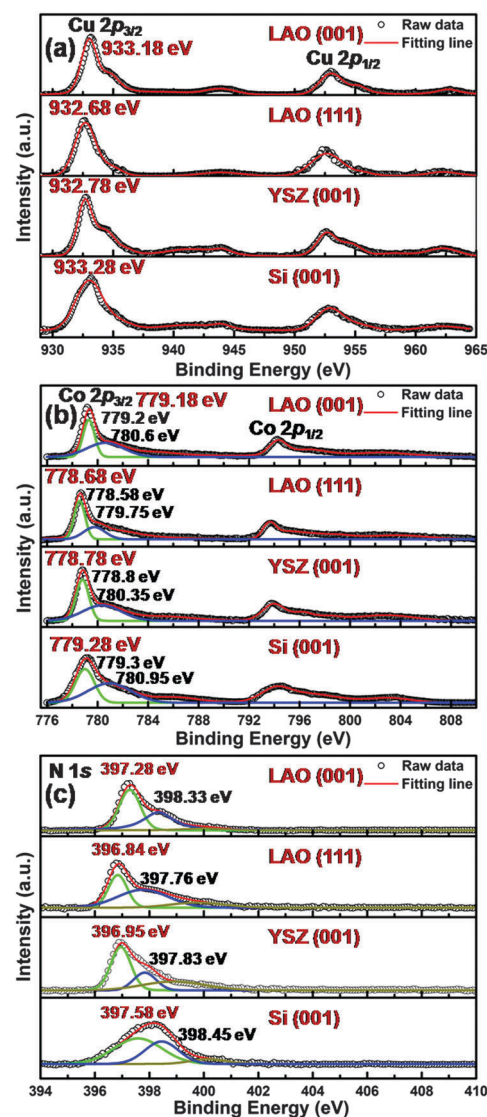


Fig. 5 XPS spectra of the derived CNC thin films (a) Cu 2p, (b) Co 2p and (c) N 1s.

reflecting the coexistence of two distinct sites for the Co atoms in the face centers, which successively resulted in different exchange-interactions between Co and N atoms, and diverse covalency of the Co 3d–N 2p hybridized bands. The face-centered atomic sites of the cubic lattice become non-equivalent due to the anisotropic characteristic of Co 3d electron orbits. The Co atoms at face-centered positions, further distinguishable in the presence of spin–orbit interaction according to the direction of their four-fold rotation axis relative to the moments, are easily hybridized with neighboring nitrogen to an extent that is strongly dependent on volume and chemical coordination.³⁶ For the N 1s core level spectra, the peak is broad and asymmetric, which can be well fitted by three curves. The stronger peak at ~ 397 eV is attributed to diverse covalency of the Cu (Co) 3d–N 2p hybridized bands, while the shoulder at ~ 398 eV is generally interpreted due to residual surface contaminants.³⁷ The N 1s peaks have a satellite structure on the higher binding-energy side, which confirms the covalency of the Cu(Co) 3d–N 2p hybridized bands.

Upon increasing the nitrogen content, the binding energy of Cu 2p_{3/2}, Co 2p_{3/2} and N 1s increases. The binding energy of Cu 2p_{3/2}, Co 2p_{3/2} and N 1s is 933.18, 779.18 and 397.28 eV for the CNC/LAO(001) thin film, 932.68, 778.68 and 396.84 eV for the CNC/LAO(111) thin film, 932.78, 778.78 and 396.95 eV for the CNC/YSZ(001) thin film and 933.28, 779.28 and 397.58 eV for the CNC/Si(001) thin film, respectively. Therefore, the nitrogen content is the highest for the CNC/Si(001) thin film, than CNC/LAO(001) and CNC/YSZ(001) thin films, and the CNC/LAO(111) thin film has the lowest nitrogen content, which is consistent with the XRD results, the more the nitrogen content, the greater the lattice constant is.

Temperature dependent magnetization M – T at high temperatures of a typical thin film CNC/LAO(001) is carried out on a vibrating sample magnetometer (VSM) and the result is shown in Fig. 6(a). It is seen that in the zero-field-cooling (ZFC) branch magnetization is gradually decreased with increasing temperature up to 650 K. However, upon further increasing the temperature, the magnetization is increased rapidly. On the other hand, in the field-cooling (FC) branch the magnetization is obviously enhanced and irreversible characteristics between the ZFC and FC curves are observed. The above-mentioned characteristics are the same as the previous report on Co_{5.47}N thin films, suggesting the decomposition of CNC when the temperature is higher than 650 K.¹⁸ Moreover, it is also suggested that the ferromagnetic Curie temperature T_c is higher than 650 K for the CuNCo₃ compound.

Fig. 6(b) shows the field dependent magnetization (M – H) loops at 300 K of all derived CNC thin films on different substrates with an applied field parallel to the film surface. According to the films thickness, the volumes of the films are obtained. It is seen that the saturation magnetization per unit volume M_s is 232 ($\sim 0.44 \mu_B/\text{Co}$), 190 ($\sim 0.36 \mu_B/\text{Co}$), 125 ($\sim 0.24 \mu_B/\text{Co}$) and 107 emu cm^{−3} ($\sim 0.20 \mu_B/\text{Co}$), while the coercivity field H_c is 48, 82, 89 and 77 Oe for CNC thin films on LAO(001), LAO(111), YSZ(001) and Si(001), respectively. Except for the CNC/Si(001) thin film, it is observed that a higher M_s is accompanied by a lower H_c , which is the same as the previous reports.^{38–42} The results of M_s as

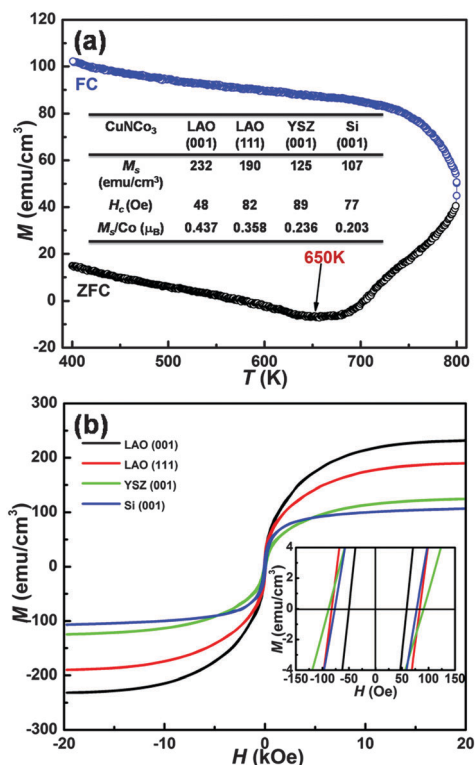


Fig. 6 (a) Temperature dependence of magnetism in FC and ZFC modes under 2000 Oe applied magnetic field parallel to the surface; the M – H loops at 300 K with the applied magnetic field parallel to the film surface for all derived CNC thin films on (b). For clarity, the inset of (a) gives the detailed parameters. The M – H curves under a low magnetic field with high resolution are displayed in the inset of (b).

well as H_c suggest that CNC thin films can be considered as a type of room temperature soft-magnet with the T_c higher than 650 K.

As for the difference in M_s for CNC thin films on LAO(001) and LAO(111) substrates, it is seen that the value is higher for the former one, which can be attributed to the higher nitrogen content in the CNC/LAO(001) thin film as discussed in previous reports.^{22,41} However, for the M_s between the samples the CNC/YSZ(001) thin film and the CNC/LAO(111) thin film, it is observed that although the nitrogen content is higher for the former one, the M_s is higher for the latter one, which suggests that N content is not at least the unique factor to determine the M_s value. As reported previously,^{38,41} it is found that an obvious decrease in M_s will occur with decreasing crystalline quality in Co₄N due to their unsaturated Co–N bonds. As shown in XRD results, it is seen that the crystalline quality as well as the FWHM of the rocking curve of CNC/LAO(111) is better than those of CNC/YSZ(001), which will lead to the higher M_s value for the former one. On the other hand, the M_s value is the lowest for the CNC/Si(001) thin film, which can be attributed to the dewetting morphology and the lowest crystalline quality. The characteristic of dewetting causes a reduction in the film mass per unit volume, due to the reason that the M_s value of the sample CNC/Si(001) will be greatly reduced.

The temperature dependence of resistivity is shown in Fig. 7 and the values corresponding to the obtained parameters are listed in Table 1. It is seen that all the samples show a

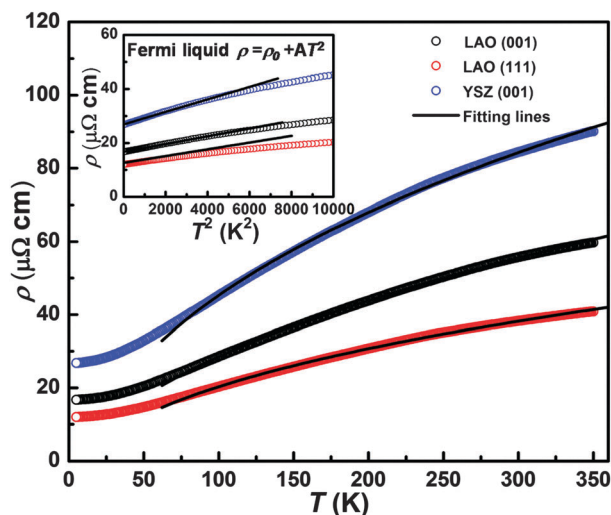


Fig. 7 Temperature dependence of resistivity of CNC thin films on LAO(001), LAO(111) and YSZ(001) substrates as well as the transport fitting results and the inset is the enlarged image to give the transport fitting results in the low T region.

Table 1 The obtained electrical parameters for all derived CuNC_3 thin films

CuNC_3	$\rho_{300\text{K}}$ ($\mu\Omega\text{ cm}$)	$T_{\text{fermi liquid}}$ range (K)	ρ_0 ($\mu\Omega\text{ cm}$)	A ($\times 10^{-3}\ \mu\Omega\text{ cm K}^{-2}$)
LAO(001)	55.7	5–69	16.7	1.44
LAO(111)	38.2	5–69	12.1	1.03
YSZ(001)	84.4	5–68	26.9	2.30

metallic behavior. According to the theoretically calculated results based on density functional theory, the density of states (DOS) near E_F is predominately contributed by the 3d electrons of Co. No band gap was observed. Thus we also calculated the DOS for different Hubbard U . Hubbard U influences the shape of DOS. However, even the very large U of 5 eV cannot open a band gap. Therefore, based on the DFT calculations, the metallic ground state of CuNC_3 is very robust and the metallic behavior is an inherent property of the samples (see ESI† for details). The resistivity within the whole measured temperature range is the lowest for the CNC/LAO(111) thin film, then the CNC/LAO(001) thin film, and the CNC/YSZ(001) thin film has the largest resistivity. The resistivity at 300 K is 38.2, 55.7 and 84.4 $\mu\Omega\text{ cm}$ for the CNC/LAO(111) thin film, the CNC/LAO(001) thin film and the CNC/YSZ(001) thin film, respectively. Due to the dewetting morphology of the CNC/Si(001) thin film the transport property is not shown here. It is seen that the $\rho_{300\text{K}}$ of the derived CNC thin films is much lower than that of other antiperovskite bulks due to the decreased grain boundary scattering of carriers. Combined with the magnetic properties and the microstructures as shown in XRD results, it is suggested that the resistivity is dominantly controlled by the microstructures, especially by the out-of-plane orientation, which suggests that the smaller value of the FWHM in the rocking curve will lead to the lower value of the resistivity.

In general, the total ρ of the films can be expressed by the equation

$$\rho(T) = \rho_0 + \rho_{\text{ph}}(T) + \rho_{\text{ee}}(T) + \rho_{\text{m}}(T), \quad (1)$$

where ρ_0 is the residual resistivity, $\rho_{\text{ph}}(T)$ is the contribution from the electron–phonon scattering process, $\rho_{\text{ee}}(T)$ is the contribution from the electron–electron scattering process, and $\rho_{\text{m}}(T)$ is the contribution from disordered localized magnetic moments.⁴¹ The electron–phonon scattering process is prominent at higher temperature. At $T \geq \theta_D$, (θ_D is the Debye temperature), ρ variation with temperature follows the simple relationship, $\rho_{\text{ph}}(T) \propto T$, and in the temperature range $T \leq \theta_D$, ρ can be written as $\rho_{\text{ph}}(T) \propto T^5$. The electron–electron interaction is prominent in the low temperature region where electron–phonon scattering is frozen out and ρ follows the $\rho_{\text{ee}}(T) \propto T^2$ law. The contribution to ρ by disordered localized magnetic moments is important in the entire temperature range and can be given by the relationship $\rho_{\text{m}}(T) \propto T^2$ for ferromagnetic coupling and T^5 & T^4 for anti-ferromagnetic coupling.⁴³ By fitting using eqn (1), however, the experimental data cannot be well fitted. On the other hand, the T^n relationship can be well fitted at high temperatures (70–350 K) with n smaller than 1, which suggests that electron–phonon scattering is the dominant factor for resistivity.⁴⁴ At the low temperatures (5–70 K), the resistivity follows the $\rho = \rho_0 + AT^2$ law, where ρ_0 is the residual resistivity and A is the Fermi liquid transport coefficient, which suggests the Fermi liquid behavior at low temperatures due to the prominent electron–electron interaction and the freezing out of electron–phonon scattering.⁴⁵ The ρ_0 is 12.1, 16.7 and 26.9 $\mu\Omega\text{ cm}$ and A is 1.03, 1.44 and 2.32 $\mu\Omega\text{ cm K}^{-2}$ for the CNC/LAO(111) thin film, the CNC/LAO(001) thin film and the CNC/YSZ(001) thin film, respectively. Combined with the microstructure results, it is suggested that the ρ_0 is dominantly controlled by the microstructures in spite of N content. The decrease in A indicates a decrease in the effective mass m^* according to dynamical mean field theory (DMFT),^{46,47} which gives that the m^* of a Fermi liquid is predicted from $A \propto (m^*)^2$.

4 Conclusions

In summary, antiperovskite CuNC_3 thin films have been prepared for the first time by chemical solution deposition on different single crystal substrates. c -axis orientation is observed for all derived thin films regardless of the orientation of the single crystal substrates, suggesting the self-assembled c -axis orientation due to the lowest surface energy of the (00 ℓ) surface. From the magnetic measurements, it is concluded that CuNC_3 can be classified into a new type of soft-magnetic material with a Curie temperature higher than 650 K. The derived thin films show metallic electronic transport properties and at high temperatures the resistivity is dominated by electron–phonon scattering, while at low temperatures the electron–electron interaction plays a very important role. The results will provide an effective route for fabricating antiperovskite cobalt-based thin films as well as provide a prototype for the investigation of the growth mechanisms of complex metal nitride thin films by solution methods.

This work was supported by the National Basic Research Program of China (2014CB931704 and 2011CBA00111) and the National Nature Science Foundation of China under Contract No. 51171177 and 11174288. Dr Peng Tong acknowledges the funding from Hefei Centre for physical science and technology under Contract No. 2012FXCX007.

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