Journal of Alloys and Compounds 582 (2014) 75–78

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

The preparation and antiferromagnetic properties of epitaxial rocksalt-type CoN films

Xiangbo Liu [a], Huibin Lu [a,*], Meng He [a], Kuijuan Jin [a], Guozhen Yang [a], Hao Ni [b], Kun Zhao [b]

[a] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[b] College of Science, China University of Petroleum, Beijing 102249, China

ARTICLE INFO

Article history:
Received 22 May 2013
Accepted 1 August 2013
Available online 14 August 2013

Keywords:
Cobalt nitrides
Epitaxial growth
Antiferromagnteic property

ABSTRACT

We have grown epitaxial rocksalt-type CoN films on $SrTiO_3$ and sapphire substrates by ablating a cobalt target in activated nitrogen atmosphere. The structural and magnetic properties have been investigated. X-ray diffraction profiles show CoN films grow along the [100] and [111] direction on $SrTiO_3(100)$ and α-$Al_2O_3(0001)$, respectively. High-resolution transmission electron microscopy measurement has been performed on CoN/$SrTiO_3$ system, which shows a good epitaxial growth. Temperature-dependent magnetization curves reveal that the as-grown films have antiferromagnetic properties with T_N of ~310 K.

The preparation and the basic magnetic properties of magnetic transition metal nitrides MN_x (M = Cr, Mn, Fe, Co, Ni) have attracted increasing attention in recent years, due to the potential application in high density magnetic recording media [1]. To date, the research on FeN_x, MnN_x, CrN_x, and NiN_x has been reported widely [2–5], whereas the study of CoN_x is relatively poor. To the best of our knowledge, although a limited number of publications have reported various phases of Co–N system such as Co_4N, Co_3N, Co_2N, Co_2N_3, and CoN, [6–10] the detailed magnetic measurements are still scarce. For example, the perovskite structure Co_4N is found to be ferromagnetic (FM) in nature, but the exact value of Curie temperature (T_C) remains unclear. With regard to Co_2N and Co_3N, the related magnetic measurements are waiting to be developed. AB-type structure is a common phase of 3d transition metal nitrides. Cobalt mononitride (CoN) has two possible crystal structures: rocksalt (RS-) type and zinc-blende (ZB-) type. An earlier work about CoN is reported by Schmitz-Dumont et al. who prepared RS-type CoN powder by the thermal decomposition of cobalt(III) amide $Co(NH_2)_3$, and found it had RS-type structure [11]. The relevant physical properties are very hard to be referred. Recently, Suzuki et al. prepared the ZB-type polycrystalline CoN film by d.c. reactive sputtering, magnetic measurements and nuclear magnetic resonance demonstrated it exhibited Pauli paramagnetic character [12,13].

In our opinion, the difficult obtainment of high quality Co–N films is the main factor that hinders the related research. Because CoN_x can stable into a wide range x, CoN_x films often comprise more than one phase [14,15]. Only a few works report the pure phase CoN_x films prepared by magnetron sputtering, molecular beam epitaxy, and nitridation of Co film [12,16,8]. In the present work, we report laser molecular beam epitaxy (Laser-MBE) is an effective way to get CoN single crystal film. The films show typical antiferromagnetic (AFM) nature with a Néel temperature (T_N) of ~310 K. The magnetic property suggests the prepared CoN films have RS-type structure rather than ZB-type.

RS-type cobalt mononitride films were grown on $SrTiO_3(100)$ and α-$Al_2O_3(0001)$ substrates by means of Laser-MBE with a XeCl excimer laser (wavelength = 308 nm, repetition = 2 Hz, and energy density = 1.5 J/cm^2). [17] A high-purity cobalt disk (purity >99.99%) was employed as target. Before deposition, gas pipes and epitaxy chamber had been carefully cleaned using high-purity N_2 (>99.999%). The epitaxy chamber was pumped to 10^{-6} Pa before nitrogen gas was introduced into the chamber, and nitrogen partial pressure was kept at 0.5 Pa. The nitrogen had been activated by a home-made glowing discharge unit and been sprayed to the substrate surface directly. The substrate temperature during the growth was maintained at 370 °C after excluding other temperature prudently. The nitrogen source was turn off after the samples were cooled down to 150 °C. The growth time was 4 h, and growth rate was estimated to be 3.3 Å/min. The thicknesses of grown films were about 80 nm.

The surface quality was monitored by *in situ* reflection high energy electron diffraction (RHEED). And the RHEED patterns were recorded after the growth. Fig. 1a and b shows two RHEED patterns of as-grown CoN film on $SrTiO_3$ substrate, in which the incident electron beam is parallel to $SrTiO_3$ [110] and [100] direction, respectively. The bright and sharp diffraction streaks indicate the

* Corresponding author. Tel.: +86 1082649350.
E-mail address: hblu@iphy.ac.cn (H. Lu).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.08.001

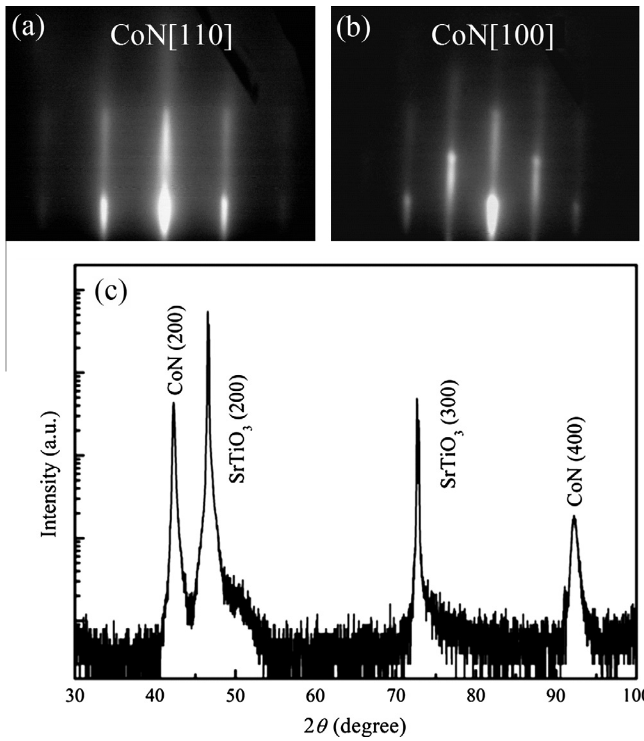

Fig. 1. (a) and (b) show RHEED patterns of as-grown CoN film on $SrTiO_3$ substrate, in which the incident electron beam is along $SrTiO_3$ [1 1 0] and [1 0 0] direction. (c) A typical θ–2θ scanning X-ray diffraction profile of CoN film on $SrTiO_3$(1 0 0).

well crystallization. But the extra spots on the streaks suggest slightly rough surface. It is noted that both RHEED patterns turn up again after rotating the substrate by 90°. The crystal structure was characterized by X-ray diffraction (XRD) using Rigaku D/Max-2400 with Cu Kα radiation. Fig. 1c displays a typical XRD θ–2θ scanning curve of CoN film on $SrTiO_3$ substrate. With the exception of two peaks ascribed to substrate, only diffraction peaks at $2\theta = 42.3°$ and 92.25° associated with CoN (2 0 0) and (4 0 0) were detected, without any diffraction signal from either randomly oriented grain or impurity phase, revealing the as-grown CoN films have highly pure crystal phase and grow along [1 0 0] direction on $SrTiO_3$(1 0 0) substrate. Using Bragg formula, the crystal constant of CoN is estimated to be $a = 4.27$ Å. This is in accord with the value of RS-type CoN powder reported in Ref. [11]. Based on the RHEED and XRD results, we can speculate that the epitaxial relationship between CoN and $SrTiO_3$ is a cube-on-cube type even the lattice mismatch is as high as $[a(\text{CoN})\text{-}a(\text{STO})]/a(\text{STO}) \times 100\% = 9.3\%$.

As mentioned previously, we know cubic CoN has two possible crystal structures: zinc-blende (ZB) type and rocksalt (RS) type. They have similar lattice constants (4.28 Å for ZB-type and 4.27 Å for RS-type) [12]. In both of these structures, Co atoms arrange into a face-centered cubic (f.c.c.) structure. The only difference is the arrangement of nitrogen atoms. So it is difficult to exactly point out the phase of the as-grown films only by θ–2θ profile. A general but nonstrict method to distinguish the two structures is to compare the relative intensity of diffraction peaks in XRD profiles due to the different structure factors [12]. But in here, this method is impracticable because the diffraction just takes place from a single crystal plane. Therefore, other measurements are highly required to indentify the film structure.

To analyze the microstructures of CoN(1 0 0)/$SrTiO_3$(1 0 0) system, high-resolution transmission electron microscopy (HRTEM) measurements were performed to the cross section using a FEI Tecnai G2 F20 microscope. (Fig. 2a) presents a cross-sectional HRTEM image of CoN/$SrTiO_3$. The interface of film/substrate is very clear and the atomic arrangement is highly ordered in the film part, which are indicative of epitaxial growth. Because of the large lattice mismatch (9.3%), several atom layers closing to the interface have to adopt distortion to achieve the epitaxial growth. The selected-area electron diffraction (SAED) pattern (in Fig. 2b) shows a very clean single crystal diffraction pattern, revealing that the as-grown CoN film has well single crystal structure, it is in good agreement with XRD measurement. The film is indexed to be a cubic structure.

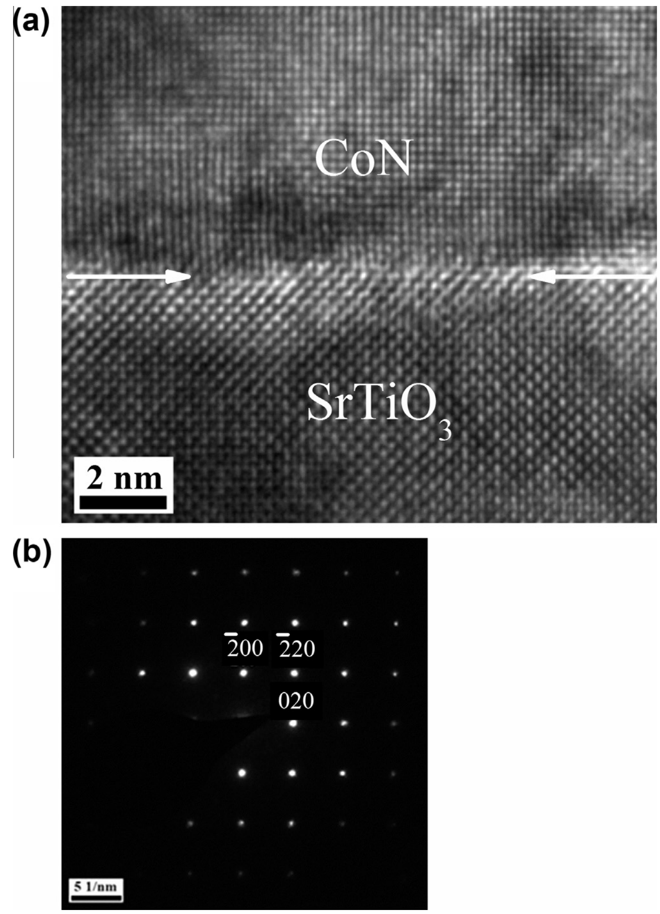

Fig. 2. (a) High-resolution cross-sectional TEM image of CoN/$SrTiO_3$ film. (b) The SAED pattern of CoN film.

Magnetic measurements were carried out with a vibrating samplemagnetometer (VSM, PPMS-9T). Zero-field-cooled (ZFC) and field-cooled (FC) d.c. magnetization measured in a temperature range of 10–400 K are plotted in Fig. 3a. External field of 0.2 and 10 kOe were applied in the plane of the film. It is very clear that each thermomagnetic (M–T) curves shows a sharp peak at the temperature of $T \sim 310$ K. We tentatively speculate that CoN film transits from high-temperature paramagnetic (PM) order to low-temperature AFM order with a Néel point of $T = 310$ K. In fact, at $T \geqslant 310$ K, the magnetizations increase gradually with the decreasing temperature, and behave in Curie–Weiss law for $1/M$ show linear temperature dependence approximately, as plotted in the inset of Fig. 3a, which is a typical characteristic for PM materials. At $T < 310$ K, the magnetizations decrease with the reducing temperature, the film transits into AFM state. It is should be noted that ZB-type CoN is Pauli paramagnetic, which is verified by nuclear magnetic resonance and magnetization measurements [12,13]. In addition, a lot of works show RS-type mononitrides of the neighboring elements of cobalt, such as CrN, MnN, FeN have typical AFM

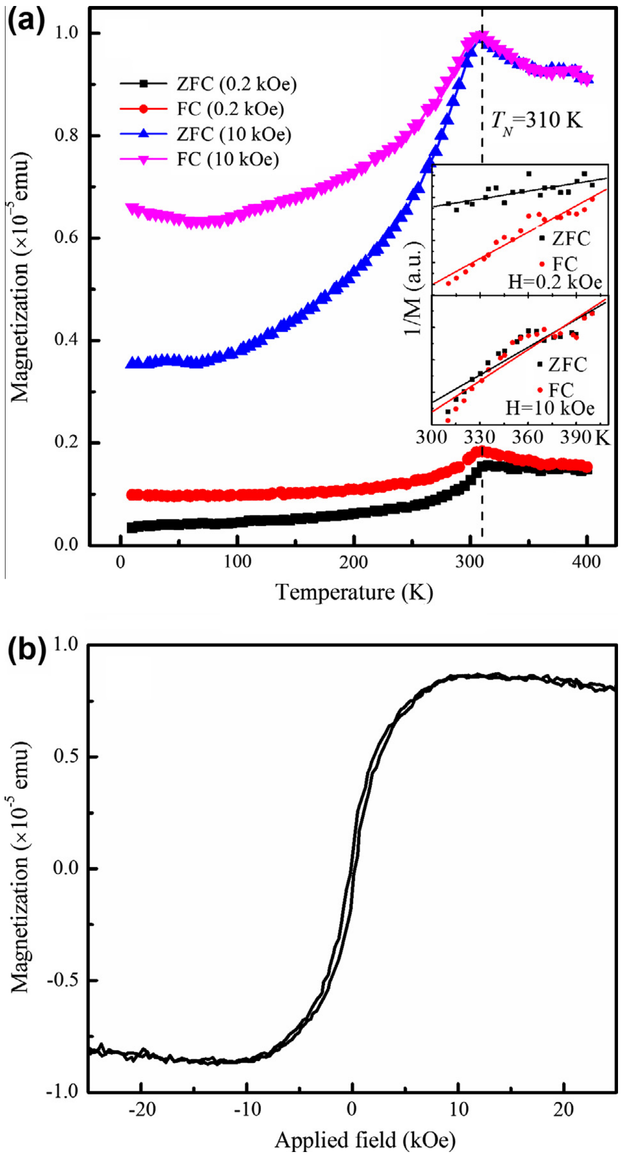

Fig. 3. (a) ZFC and FC magnetization of CoN(100)/$SrTiO_3$(100) from 10 to 400 K measured at 0.2 and 10 kOe field. The insets show the value of $1/M$ in the temperature range of 310–400 K, solid lines are fitting results by Curie–Weiss law. (b) M–H loop of CoN(100)/$SrTiO_3$(100) measured at 300 K.

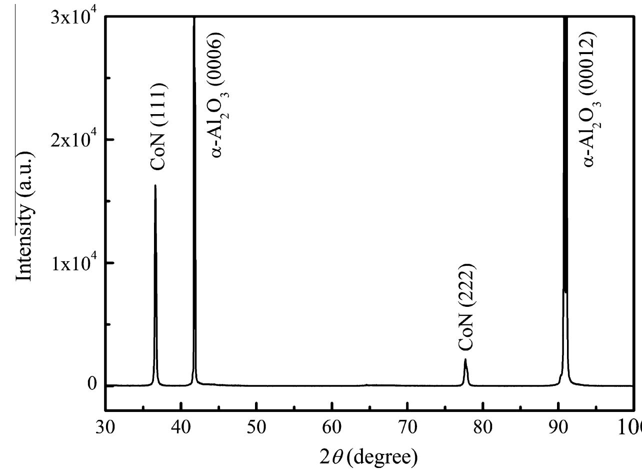

Fig. 4. A θ–2θ scanning X-ray diffraction profile of CoN(111) film on α-Al_2O_3(0001).

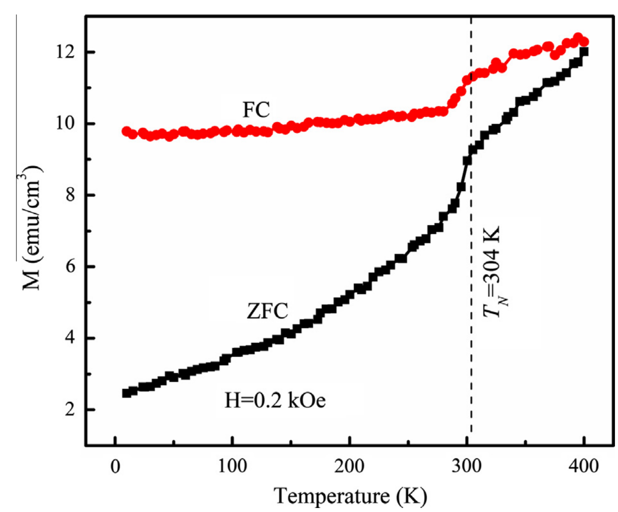

Fig. 5. Temperature-dependent magnetization curves of CoN(111)/α-Al_2O_3(0001) measured at 0.2 kOe field.

properties [18–20]. Phase transition is one of the most important intrinsic characteristics of a material. Therefore, we can conclude that the as-prepared CoN films should not be ZB-type structure, but be RS-type structure because of their AFM property.

The field-dependent magnetization (M–H) loop is plotted in Fig. 3b measured at 300 K, with an applied field parallel to the film plane. One can see a very weak ferromagnetic-like magnetic hysteresis. We tentatively ascribe it to the interfacial structures, or ferromagnetic defects, such as Co_4N and α-Co. It is more likely to form nonstoichiometric CoN_x clusters during the growth process due to the partial uncompleted nitridation.

CoN films have also been grown on *c*-plane sapphire substrates under the same conditions as grown on $SrTiO_3$ substrates. Fig. 4 plots a θ–2θ XRD profile of CoN/Al_2O_3 system. The film shows two peaks at $2\theta = 36.6°$ and 77.7° corresponding to (111) and (222) of cubic CoN. No other peak is observed, indicating that CoN film orients in [111] direction when grows on α-Al_2O_3(0001) substrate.

Fig. 5 shows ZFC and FC M–T curves of CoN(111) film on α-Al_2O_3(0001) substrate measured from 10 to 400 K, with a 0.2 kOe field along the film plane. Unlike CoN/$SrTiO_3$ system, sharp peaks have not been observed on the M–T curves. One can see the magnetization decreases monotonously with the reducing temperature, but an obvious hop appears at $T = 304$ K on every M–T curve which corresponds to the Néel point. At $T > 304$ K, it is very clear that the magnetization does not obey the Curie-Weisis law. We attribute the anomalous phenomenon to the different interface strain, different crystal direction, and crystal defects.

In conclusion, cubic RS-type CoN epitaxial films have been grown on $SrTiO_3$(100) and α-Al_2O_3(0001) substrates by Laser-MBE with activated nitrogen. RHEED, XRD, and HRTEM measurements have been employed to characterize the structure of CoN(100) films grown on $SrTiO_3$(100). These results confirm the good crystal quality and well epitaxial growth of CoN(100) films. Magnetic measurement indicates a PM-to-AFM transition takes place at $T_N \sim 310$ K. This property suggests the as-prepared films are not Pauli paramagnetic ZB-type CoN, but AFM RS-type structure. However, the interface structures and defects may lead to the ferromagnetic-like hysteresis phenomenon. CoN film grows on α-Al_2O_3(0001) is in the [111] direction, and its AFM order temperature is ∼304 K.

Acknowledgements

The authors thank Prof. Guangheng Wu for his helpful discussion on the results of magnetic measurement. This work was supported by the National Basic Research Program of China (Projects No. 2010CB630704 and 2012CB921403).

References

[1] J.M.D. Coey, P.A.I. Smith, J. Magn. Magn. Mater. 200 (1999) 405.
[2] X. Wang, W.T. Zheng, H.W. Tian, S.S. Yu, W. Xu, S.H. Meng, X.D. He, J.C. Han, C.Q. Sun, B.K. Tay, Appl. Surf. Sci. 220 (2003) 30.
[3] W.R.L. Lambrecht, M. Prikhodko, M.S. Miao, Phys. Rev. B 68 (2003) 174411.
[4] C. Constantin, M.B. Haider, D. Ingram, A.R. Smith, Appl. Phys. Lett. 85 (2004) 6371.
[5] D. Vempaire, S. Miraglia, A. Sulpice, L. Ortega, E.K. Hlil, D. Fruchart, J. Pelletier, J. Magn. Magn. Mater. 272–276 (2004) E843.
[6] K. Suzuki, T. Kanedo, H. Yoshida, H. Morita, H. Fujimori, J. Alloy. Comp. 224 (1995) 232.
[7] C.W. Su, M.S. Huang, Y.C. Chang, T.H. Tsai, Y.H. Lee, J.C. Lee, J. Appl. Phys. 105 (2009) 033509.
[8] M. Hasegawa, T. Yagi, Solid State Commun. 135 (2005) 294.
[9] W. De La Cruz, O. Contreras, G. Soto, E. Perez-Tijerina, Rev. Mex. Fís. 52 (5) (2006) 409.
[10] J.S. Fang, L.C. Yang, C.S. Hsu, G.S. Chen, Y.W. Lin, G.S. Chen, J. Vac. Sci. Technol., A 22 (3) (2004) 698.
[11] O. Schmitz-Dumont, N. Kron, Angew, Chem. 67 (1955) 231.
[12] K. Suzuki, T. Kanedo, H. Yoshida, Y. Obi, H. Fujimori, H. Morita, J. Alloy. Comp. 306 (2000) 66.
[13] K. Suzuki, T. Shinohara, F. Wagatsuma, T. Kaneko, H. Yoshida, Y. Obi, S. Tomiyoshi, J. Phys. Soc. Jpn. 72 (2003) 1175.
[14] K. Oda, T. Yoshio, K. Oda, J. Mater. Sci. 22 (1987) 2729.
[15] H. Asahara, T. Migita, T. Tanaka, K. Kawabata, Vacuum 62 (2001) 293.
[16] K. Ito, K. Harada, K. Toko, M. Ye, A. Kimura, Y. Takeda, Y. Saitoh, H. Akinage, T. Suemasu, Appl. Phys. Lett. 99 (2011) 252501.
[17] G.Z. Yang, H.B. Lu, F. Chen, T. Zhao, Z.H. Chen, J. Cryst. Growth 227–228 (2000) 929.
[18] L.M. Corliss, N. Elliott, J.M. Hastings, Phys. Rev. 117 (1960) 929.
[19] B.R. Saha, Leonard Kleinman, Phys. Rev. B 68 (2003) 113101.
[20] T. Hinomura, S. Nasu, Phys. B 237–238 (1997) 557.