Emergent Magnetic States and Tunable Exchange Bias at 3d Nitride Heterointerfaces

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Interfacial magnetism stimulates the discovery of giant magnetoresistance (MR) and spin–orbital coupling across the heterointerfaces, facilitating the intimate correlation between spin transport and complex magnetic structures. Over decades, functional heterointerfaces composed of nitrides have seldom been explored due to the difficulty in synthesizing high-quality nitride films with correct compositions. Here, the fabrication of single-crystalline ferromagnetic Fe₃N thin films with precisely controlled thicknesses is reported. As film thickness decreases, the magnetization dramatically deteriorates, and the electronic state changes from metallic to insulating. Strikingly, the high-temperature ferromagnetism is maintained in a Fe₃N layer with a thickness down to 2 u.c. (≈8 Å). The MR exhibits a strong in-plane anisotropy; meanwhile, the anomalous Hall resistivity reverses its sign when the Fe₃N layer thickness exceeds 5 u.c. Furthermore, a sizable exchange bias is observed at the interfaces between a ferromagnetic Fe₃N and an antiferromagnetic CrN. The exchange bias field and saturation moment strongly depend on the controllable bending curvature using the cylinder diameter engineering technique, implying the tunable magnetic states under lattice deformation. This work provides a guideline for exploring functional nitride films and applying their interfacial phenomena for innovative perspectives toward practical applications.

1. Introduction

Magnetic materials possessing ultralarge remanent magnetization and small coercive fields are generally useful in the magnetic recording and energy harvest industries, such as motors, generators, and actuators. Typically, Fe–Co alloys and compounds containing rare-earth elements (such as Sm and Nd) historically have been chosen for the beforehand applications. However, the cost of manufacturing and maintaining such materials is too high for developing highly efficient, compact, and reliable devices for future technologies. Transition metal nitrides (TMNs) are a class of functional materials in which the nitrogen atoms are integrated into the interstitial sites of parent metals. Therefore, TMNs exhibit extremely rich physical properties, for instance, high dielectricity, high thermal conductivity, superconductivity, ferroelectricity, as well as...
magnetism.\textsuperscript{[27–29]} Except for these remarkable physical properties, the characteristics of superior hardness, corrosion resistance, and antioxidant have made TMNs stable in the air and suitable for coating layers of functional devices.\textsuperscript{[1–3]} Although TMNs have many advantages, the challenges in synthesizing single-crystalline TMN thin films with high crystallinity and correct chemical composition have hindered the research on their intrinsic properties and intriguing interfacial phenomena. Taking iron nitrides as an example, Fe\textsubscript{6}N\textsubscript{2} has been theoretically predicted as one of the most promising rare-earth-free strong magnet candidates with a giant saturation moment ($\approx 3.5 \mu_B$/Fe), which is 36% larger than that of a single-crystal iron ($\approx 2.2 \mu_B$/Fe).\textsuperscript{[20,21]} Increasing the nitrogen content, Fe\textsubscript{3}N exhibits ferromagnetism with a slightly reduced saturation moment. Due to its ultralarge spin polarization, it holds potential applications in magnetic tunneling junctions and spin-polarized light-emitting diodes.\textsuperscript{[22–27]} However, Fe\textsubscript{3}N often appears in other iron nitride forms due to the close thermally stable energy. The magnetic and electrical properties of Fe\textsubscript{3}N can be greatly influenced by impurities, chemical disorders, and nitrogen vacancies (NVs).\textsuperscript{[28]} Currently, most work mainly focuses on amorphous, polycrystalline, and nanoparticle nitrides.\textsuperscript{[22–28]} The sample quality hinders the deep investigation of their intrinsic properties in their thin film form. Therefore, mastering the advanced preparation methods of TMN magnetic films with the accurate stoichiometric ratio is particularly important to understand the structure of objective substances and investigate the coupling mechanism between spin and other degrees of freedom. These factors are the core constraints restricting the practical applications of these excellent magnetic materials.

Previously, most TMN thin films were fabricated by reactive magnetron sputtering, radiofrequency nitrogen plasma-assisted molecular beam epitaxy, or metal–organic chemical vapor deposition.\textsuperscript{[29–35]} The crystallinity is relatively poor because of the formation of polycrystalline grains and NVs. Recently, our group reported the fabrication of high-crystalline stoichiometric CrN ultrathin films using the pulsed laser deposition (PLD) technique.\textsuperscript{[32–35]} The specimens were prepared by laser abating from a high-pressure synthesized stoichiometric target and compensating the NVs using an in situ atomic nitrogen plasma source. The CrN thin films fabricated in this manner exhibited a paramagnetic-to-antiferromagnetic transition at a temperature close to its bulk value $\approx 283$ K,\textsuperscript{[36,37]} indicating the correct stoichiometry of high-quality CrN films. Thus, depending on the thickness, orientation, stacking sequence, and emergent interfacial phenomena, their intrinsic physical properties could be explored in a controlled manner,\textsuperscript{[32–35]} similar to the extensively investigated transition metal oxides.

In this work, we report the fabrication of stoichiometric single-crystalline Fe\textsubscript{3}N thin films and the integration of antiferromagnetic CrN films with atomically sharp interfaces. The thickness-dependent magnetic and electrical phase transitions were observed. When the thickness was reduced to 2 unit cells (u.c.), the ferromagnetic ground state of a Fe\textsubscript{3}N film was maintained. We observed a significant anomaly in the out-of-plane magnetic hysteresis loops depending on the film thickness and temperature, which may be attributed to the reorientation of canted spins. We noted that the magnetic properties of a freestanding Fe\textsubscript{2}N/CrN bilayer were extremely sensitive ($\approx 2680$ emu cm$^{-1}$ per mm$^3$) to the bending stress, providing an innovative design strategy for uniaxial-strain sensors.

2. Results and Discussion

The nitridation of iron leads to a variety of phases, strongly depending on the nitrogen content. Among them, $\varepsilon$-phase Fe\textsubscript{3}N ($\varepsilon$-Fe\textsubscript{3}N, abbreviation Fe\textsubscript{3}N thereafter) exhibits interesting magnetic states and extends over a wide range of the phase diagram.\textsuperscript{[38]} A typical crystallized form of Fe\textsubscript{3}N is presented in Figure 1a. A succession of Fe–N layers is arranged along the c axis with N layers as spacers between Fe layers, resulting in an out-of-plane lattice constant of 4.38 Å. When viewed from the [001] direction, Fe\textsubscript{3}N consists of alternating atomic planes of Fe$^{3+}$ and N$^{3-}$ ions with a buckled hexagonal structure (Figure 1b). The atomic arrangement of Fe\textsubscript{3}N is similar to that of a (001) surface of $\alpha$-Al$_2$O$_3$ (point group $R\overline{3}m$) (Figure 1c). The lattice constants of Fe\textsubscript{3}N and $\alpha$-Al$_2$O$_3$ are very close, yielding a moderate lattice mismatch of $\approx 1.8\%$. The similar crystal symmetry and relatively small lattice mismatch enable the epitaxial fabrication of $\varepsilon$-phase Fe\textsubscript{3}N films on the $\alpha$-Al$_2$O$_3$ substrates using the plasma-assisted PLD technique. The highly reactive N atoms in situ generated by a radio-frequency plasma source compensate the NVs during the growth. This process guarantees the correct stoichiometry of Fe\textsubscript{3}N films. Microstructures around the interfaces between Fe\textsubscript{3}N and $\alpha$-Al$_2$O$_3$ are shown in Figure 1d, performed by scanning transmission electron microscopy (STEM) in the high-angle annular dark-field (HAADF) mode. The STEM image indicates the high crystallinity of Fe\textsubscript{3}N single layers, and the sample is free of obvious defects. The HAADF-STEM image confirms the epitaxial growth of Fe\textsubscript{3}N on the substrates with atomically sharp interfaces. To note, we observed an ultrathin transition layer with a thickness of $\approx 1$ nm (marked in yellow arrows) between Fe\textsubscript{3}N and $\alpha$-Al$_2$O$_3$. This fact can be attributed to the accommodation of misfit strain. The Fe\textsubscript{3}N films need to preserve a structural transition to their lattice; thus, building up a slightly disordered region between film and substrate. Nevertheless, the overall Fe\textsubscript{3}N structure was well-maintained without hinting at severe structural disorders or impurity phases within the films. Detailed information about the transition layer can be further understood by more extensive studies utilizing elemental-specific atomic resolution electron energy loss spectroscopy (EELS), which we leave out as an important future study. The inset of Figure 1d on the upper right shows the high-magnified STEM image of a region in Fe\textsubscript{3}N. The bright features indicate the positions of Fe atom columns, matching well with the atomic structure of single-phase $\varepsilon$-Fe\textsubscript{3}N.\textsuperscript{[39]} The light element N cannot be observed clearly in these STEM images due to the small atomic number ($Z$).

X-ray diffraction (XRD) measurements were carried out on a Panalytical MRD diffractometer equipped with a monochromator (only K$_\alpha_1$ is allowed, $\lambda = 1.54$ Å). The film thickness was controlled by counting the number of laser pulses, further confirmed by X-ray reflectivity (Figure S1, Supporting Information). Figure 1e shows the XRD $\theta$–$2\theta$ scans for a 30-u.c.-thick Fe\textsubscript{3}N on $\alpha$-Al$_2$O$_3$ substrates. Only 00l reflections from both films and
substrates were observed, suggesting the epitaxial growth of Fe₃N films. The inset of Figure 1e presents a reciprocal space map around substrates’ 006 reflections. The clear Kiessig fringes up to three orders together with a narrow rocking curve at Fe₃N 002 reflection with full width at half maximum of ≈0.03° (not shown) indicate the high crystallinity of as-grown Fe₃N films. We determined that the out-of-plane lattice constant of a 30-u.c.-thick Fe₃N was ≈4.38 Å, close to its bulk value. Also, the lattice constant did not vary greatly, further decreasing the layer thickness to 10 u.c. The relaxation of epitaxial misfit strain is attributed to the sharp structural transition at interfaces by forming a nanometer-thick transition layer (Figure 1d). XPS analysis of Fe₃N films was carried out by investigating N 1s (Figure 1f) and Fe 2p (Figure 1g) core level spectra. The binding energy was carefully calibrated by taking C 1s peak at 284.6 eV as a reference. Only one main peak centered at 397.4 eV was observed, corresponding to N 1s state due to the N content in Fe₃N. The prominent components of Fe 2p peaks at 710 and 725 eV indicate hybridization between Fe and N. We notice that there were two weak pre-peaks at 706 and 720 eV, which may be associated with metallic unbonded Fe termination layers on the top surface.[40]

The magnetic and electrical transport properties of Fe₃N films were investigated as a function of film thickness. Figures 2a and 2b show the temperature-dependent magnetization (M) and resistivity (ρ) of 6-u.c.- and 30-u.c.-thick Fe₃N films, respectively. M–T and ρ–T curves for Fe₃N single films with various film thicknesses are shown in Figure S2, Supporting Information. Thickness-dependent Curie temperature (T_C), saturation moment (M_S), and ρ₁₀₀₀K are summarized in Figures 2e–g, respectively. T_C of a 30-u.c.-thick Fe₃N film was ≈440 K and reduced to ≈385 K for a 2-u.c.-thick Fe₃N film. Accompanied by the T_C reduction, M_S of Fe₃N films was dramatically reduced by decreasing the thickness below 10 u.c. (Figure 2c). Surprisingly, we found that M_S of a 2-u.c.-thick Fe₃N film was ≈150 emu cm⁻³. In fact, this saturation moment...
at subnanometer thickness is much larger than those of most correlated magnetic oxides and nitride films. The Fe$_3$N film growth with a thickness below 2 u.c. is relatively challenging because of the nitrogen-to-oxygen substitutions at the surface. The Fe oxidization would result in a possible ferromagnetic state change of Fe$_3$N to the antiferromagnetic state of Fe$_2$O$_3$. This reaction seems unavoidable without a proper capping layer. For the transport behavior of Fe$_3$N films, we observed a clear metal-to-insulator transition by decreasing the film thickness. For a 30-u.c.-thick Fe$_3$N single film, a metallic phase was maintained at all temperatures. Please note that $\rho_{300K}$ of a 30-u.c.-thick Fe$_3$N was only 9.5 $\mu\Omega$ cm, comparable to those of most noble metals, for instance, Pt ($\rho_{300K} = 10.6 \mu\Omega$ cm) and Au ($\rho_{300K} = 2.2 \mu\Omega$ cm). However, when the thickness fell below 10 u.c., the Fe$_3$N films were changed into an insulator with a sharp resistivity increase by four orders of magnitude. The dimensional confinement-induced metal-to-insulator transition has been reported previously in both correlated oxides and nitrides. Many mechanisms have been proposed to explain the critical thickness for metallic conduction, including local structural distortion, interfacial charge imbalance, or orbital ordering. In our case, a plausible interpretation of this phenomenon was weak localization, where quantum interference of electronic waves diffusing around impurities enhanced

Figure 2. Thickness dependent magnetic and transport properties of Fe$_3$N single films. a,b) Temperature-dependent magnetization and resistivity of 6-u.c.- and 30-u.c.-thick Fe$_3$N films, respectively. c,d) Field-dependent magnetization of 6-u.c.- and 30-u.c.-thick Fe$_3$N films when magnetic field is applied along in-plane ($H//ab$) and out-of-plane ($H//c$) direction, respectively. e) Curie temperature ($T_c$), f) room-temperature saturation magnetization ($M_s$), and g) resistivity ($\rho$) as a function of Fe$_3$N film thickness. h,i) MOKE images for a 30-u.c.-thick Fe$_3$N film with magnetic fields applied along the in-plane and out-of-plane direction at room temperature, respectively. The dark contrast represents the magnetization along the $-y$ (or $-z$) axis, and light contrast represents the magnetization along the $y$ (or $z$) axis when the magnetic field is applied along the in-plane (or out-of-plane) direction.
backscattering and thus led to a conductivity reduction. We modeled the low-temperature transport property of a 6-u.c.-thick \( \text{Fe}_3\text{N} \) film. It can be well-described using variable-range hopping conduction mechanism involving electron–electron interactions.\(^{46}\) In this ultrathin limit, although many Fe atoms persist in the \( \text{Fe}_3\text{N} \) films, the conducting environment is different from a bulk-like environment for nearest-neighbor hopping along the surface normal direction, ultimately driving its conductivity to the incipient order of the 2D limit.

The magnetic easy-axis of \( \text{Fe}_3\text{N} \) films aligned in the film plane, similar to most strongly correlated thin films. The coercive field (\( H_C \)) increased on film thickness reduction (Figure 2c). Figure 2d shows the magnetic hysteresis loops of 6-u.c.- and 30-u.c.-thick \( \text{Fe}_3\text{N} \) films when \( H//c \). We observed a consistent anomaly in all \( M//H \) loops of \( \text{Fe}_3\text{N} \) films with different film thicknesses. As sweeping magnetic fields from positive to negative values, the moment first linearly reduced and then abnormally increased at \( 0.2 \) T. As the magnetic field was further reduced, the moment decreased monotonically. This behavior has seldom been observed in other magnetic TMN thin films.

To ensure consistency, we record this anomaly in the \( M//H \) loops of a 30-u.c.-thick \( \text{Fe}_3\text{N} \) film as a function of temperature (Figure S3, Supporting Information). The maximum moment at \( 0.2 \) T, as well as the coercive field, continuously decreased as temperature increased. We performed the magneto-optical Kerr effect (MOKE) measurements on a 30-u.c.-thick \( \text{Fe}_3\text{N} \) film. Figures 2h and 2i show two typical field-dependent evolutions of magnetic domain patterns captured by MOKE when \( H//ab \) and \( H//c \), respectively. The white areas represent the magnetic domains, with a negative magnetization (\( M<0 \)) created by applying a negative field to positively saturated films with \( M>0 \) (black areas). The density of effective nucleation sites in our films was relatively low, indicating a rather high homogeneity of samples. Please note that the switching field along the in-plane direction was an order of magnitude smaller than that along the out-of-plane direction. Therefore, we hypothesized that the anomaly in \( M//H \) loops (\( H//c \)) was attributed to the reorientation of Fe spins from in-plane to out-of-plane through a metastable state, where the partial magnetic domains aligned in the film plane during field-switching. The magnetoresistance (MR) of 6 u.c.- and 30-u.c.-thick \( \text{Fe}_3\text{N} \) films were measured as a function of temperature and magnetic field (Figures S4–S6, Supporting Information). MR of both samples exhibited the butterfly hysteresis loops at small fields, which are coupled with \( H_C \) as comparatively shown in Figure 2c.d. Comparing MR at high fields indicates that both \( \text{Fe}_3\text{N} \) films had negative linear responses that increased systematically in magnitude with temperature decrement. Interestingly, we observed a strong in-plane anisotropy in MR strongly depending on the current direction when \( H//c \). For a 30-u.c.-thick \( \text{Fe}_3\text{N} \) film, the MR(\( I//a \)) was opposite to MR(\( I//b \)). However, when the thickness of \( \text{Fe}_3\text{N} \) films was reduced to 6 u.c., MR trends for both current directions were similar. We believe that the interesting magnetotransport behaviors were caused by the anisotropic spin alignments confined by its lattice structure. These results are consistent with the typical results for ferromagnets possessing strong in-plane anisotropy.

Furthermore, we investigated the magnetic exchange coupling at the interfaces between ferromagnetic \( \text{Fe}_3\text{N} \) and antiferromagnetic \( \text{CrN} \) layers. Figure 3a shows the HAADF-STEM image of a \( \text{Fe}_3\text{N}/\text{CrN} \) bilayer. The bright layer indicates the \( \text{Fe}_3\text{N} \) layer, while the dark layer is the \( \text{CrN} \) layer because the scattering intensity of the HAADF-STEM image was approximately proportional to the square of the atomic number, and meanwhile, the stacking density was higher in the \( \text{Fe}_3\text{N} \) layer. This result reveals that both layers were flat and continuous over long lateral distances, suggesting the formation of high-quality interfaces. The high-magnification image around the \( \text{Fe}_3\text{N}/\text{CrN} \) interface (Figure 3b) and compositional EELS maps (Figure 3c–f) obtained from the analysis of the Fe \( L_{2,3} \), Cr \( L_{2,3} \), N K-, and O K-edge signals revealed both layers that were epitaxially grown and chemically uniformed, as well as the interfaces that were atomically sharp and contained negligible chemical intermixing. The chemical and magnetization distributions across the entire sample were first examined using the polarized neutron reflection (PNR) technique. The measurements were conducted at 10 K after field cooling at 1 T from room temperature. The specular neutron reflectivities are plotted in Figure 3g as a function of wave factor (\( q=4\sin\theta/\lambda \) for the spin-up (\( R^\uparrow \)) and spin-down (\( R^\downarrow \)) polarized neutrons, where \( \theta \) is the incident angle, and \( \lambda \) is the wavelength of incident neutrons. The solid lines are the best fits to the experimental data (open symbols). The figure of merit (FOM) of PNR fit yields a value of 1.89. Figure 3h shows the calculated spin asymmetry and its corresponding fit, from which the chemical (Figure 3i) and magnetization (Figure 3j) depth profiles can be obtained. The atomic density of the \( \text{Fe}_3\text{N} \) layer was larger than that of the \( \text{CrN} \) layer. We found that the \( \text{CrN} \) layer was separated into two parts: an interface layer and a top layer. The density of the \( \text{CrN} \) interface layer was slightly smaller than its bulk value. This is possibly due to the strain compensation between dissimilar structural materials. The magnetic depth profile indicates that the \( \text{Fe}_3\text{N} \) layer exhibited a large magnetization (\( \approx1000 \) emu cm\(^{-3} \)) and slightly deteriorated when it was close to the \( \text{CrN} \) layer. We also noticed that the \( \text{CrN} \) interface layer showed a small net moment of \( \approx54 \) emu cm\(^{-3} \) after field cooling. The existence of nonzero moment in the \( \text{CrN} \) interface layer was robust because the PNR fit with the constraint of zero or negative \( M \) in the \( \text{CrN} \) interface layer had a large deviation from the experiment data, yielding FOM of 4.3 and 5.6, respectively. The field-cooled PNR data suggest that the \( \text{CrN} \) interface layer was magnetized due to the spins of \( \text{Cr} \) ions and were pinned to those of \( \text{Fe} \) ions during the field cooling.\(^{49,50} \) The magnetization integrated over the entire depth profile obtained from PNR was in good quantitative agreement with the magnetometry data.

The unique transport properties were measured across the \( \text{Fe}_3\text{N}/\text{CrN} \) interfaces from \( \langle \text{CrN} \rangle_n/\langle \text{Fe}_3\text{N} \rangle_n \text{C}_{m/4} \text{F}_3 \) superlattices, where \( n \) represents the number of unit cells of \( \text{Fe}_3\text{N} \) and \( \text{CrN} \) layers, and five is the stacking periodicity of superlattices. Prior to the transport measurements, we performed the room-temperature PNR measurements on two representative \( \text{C}_{1/4} \text{F}_3 \) and \( \text{C}_{1/4} \text{F}_9 \) superlattices (Figures S7 and S8, Supporting Information). These results demonstrated the uniformities of chemical and magnetization distributions within \( \text{Fe}_3\text{N} \) layers. The averaged saturation magnetization of \( \text{Fe}_3\text{N} \) layers in \( \text{C}_{1/4} \text{F}_3 \) was nearly identical to those of \( \text{Fe}_3\text{N} \) layers in \( \text{C}_{1/4} \text{F}_9 \). MR of \( \text{C}_{1/4} \text{F}_9 \) superlattices was recorded by applying currents along the \( a \) and \( b \) directions at various temperatures. Figure 4a–f
shows MRs at 10 K when $H//c$. We noticed that MR did not show a significant difference as a function of the applied field when $n$ was below 5 u.c. However, when $n$ was beyond 5 u.c., the degeneracy of MR between two current directions appeared. Figure 4g,h shows the contour plots of MR when $I//a$ and $I//b$ as a function of layer thickness and temperature. At low temperatures, the MR changed from negative to positive values at a critical thickness ($t$), and $t$ reduced as further the temperature increased. The strong temperature dependency in MR became subtle for thick layers. Furthermore, we also measured the Hall resistivity ($\rho_{xy}$) of $C_n/F_n$ superlattices when $H//c$ to probe the intriguing magnetic properties across the interfaces. We subtracted the ordinary Hall resistivity ($R_0H$) from $\rho_{xy}$ to separate the anomalous Hall effect (AHE) from Hall resistiv. Figure 4i–n shows the field-dependent ($\rho_{xy} - R_0H$) from $C_n/F_n$ superlattices at 10 K. A saturation ($\rho_{xy} - R_0H$) appeared for each $C_n/F_n$ superlattice above a critical field. For $n = 2–4$, the square-like open hysteresis loops were observed, but the ($\rho_{xy} - R_0H$) value was negative. When $n$ was above 5, we observed a sign reversal from negative to positive in ($\rho_{xy} - R_0H$) at 3 T. As further $n$ increased, ($\rho_{xy} - R_0H$) increased approximately linearly. Since the saturation magnetizations were almost identical in
C_{n}/F_{m} \ (n > 5) \ superlattices, we attributed that the thickness-driven AHE signal reversal possibly originated from the band topology (e.g., the number of crossing points) and was associated with k-space Berry curvature.\[51]\] However, we did not observe the typical hump-like topological Hall signals existing in other ferromagnetic metallic systems.\[52]\] Figure 4o shows the \((\rho_{xy} - R_0 H)\) reduced toward zero as gradually increasing temperature for all C_{n}/F_{m} superlattices. Temperature-driven AHE reduction can be understood by the slight Fermi level shift with respect to the avoided band crossing points. It is worth noting that the present spatial magnetic measurements could not detect sub-micrometer-scale magnetic domains (e.g., chiral magnetic bubble-like or skyrmions) in Fe_{3}N single films or C_{n}/F_{m} superlattices across the critical thickness. Further measurements using either magnetic force microscopy or Lorentz transmission electron microscopy are needed to identify the nanoscale magnetic domains and possible existing room-temperature skyrmions in such systems.

Besides the intriguing thickness-sensitive magnetotransport behaviors toward the spintronic applications, we further demonstrated that the exchange coupling across the Fe_{3}N/CrN interface was highly tunable to the mechanical bending stress. We fabricated the Fe_{3}N/CrN freestanding membranes using water-soluble single-crystalline sodium chloride substrates. We first compared the saturation moment of an as-grown Fe_{3}N/CrN bilayer on a rigid substrate and a bilayer membrane. A slight increment of the moment of \(\approx 100\) emu cm\(^{-2}\) in the Fe_{3}N/CrN membrane was attributed to the removal of substrate constraint. The Fe_{3}N/CrN membranes attached firmly to the sapphire cylinders with predetermined curvatures ranging from 0 to 0.25 mm\(^{-1}\). The variations of bending curvature led to the successful tuning of lattice deformation.\[56–58\] We could deliver a roughly linear relationship between the bending stress and the cylinder curvature (R). The membrane support on cylinders with larger R will suffer from a larger lattice deformation. Figure 5a shows \(M-H\) loops of an as-grown Fe_{3}N/CrN membrane with \(R = 0\) at 10 K. The magnetic hysteresis exhibited open loops with its center shifted to negative (positive) fields by an exchange bias field \(H_{EB}\) of \(\approx 115\) Oe after 3 T (\(-3\) T) field cooling from room temperature. This behavior suggests the presence of exchange coupling in the antiferromagnetic/ferromagnetic systems. As R increases from 0 to 0.25 mm\(^{-1}\), \(H_{EB}\) increased from 115 to 350 Oe, whereas the magnitude of \(M_S\) dramatically reduced from 950 to 280 emu cm\(^{-2}\) (Figure 5b–d). The ratio between the bending curvatures and \(M_S\) was \(\approx 2680\) emu cm\(^{-2}\) per mm\(^{-1}\), demonstrating a significant advantage of applying such a system for detecting microdeformations. Figures 5e and 5f summarizes the curvature- and temperature-dependent \(H_{EB}\) and \(M_S\), respectively. We found that \(H_{EB}\) reduced with increasing temperature and reached zero value at the blocking temperature \(T_B\) \(\approx 150\) K (Figure S9, Supporting Information), consistent with the \(T_B\) of antiferromagnetic CrN layers.\[32–35\] The transition temperature of \(H_{EB}\) shifted to a high temperature as R increases. This strategy provides a convenient

**Figure 4.** Electrical transport across the [(CrN)\(_n/\)(Fe_{3}N)\(_m\)] (C\(_{n}F_{m}\)) interfaces, where \(n\) represents the number of unit cells in the individual layer. a–f) Magnetoresistance (MR) of C\(_{n}F_{m}\) superlattices as a function of magnetic field at 10 K. The magnetic fields were applied perpendicular to the film plane. The currents were applied in parallel to a (solid symbols) and b (open symbols) orientations. g,h) MR as a function of temperature and unit cell numbers when the current was applied in parallel to a and b orientation, respectively. i–n) Anomalous Hall resistivity \(\rho_{xy}\) (solid symbols) and \(\rho_{xx}\) (open symbols) as a function of magnetic field at 10 K. o) \(\rho_{xy} - R_0 H\) as function of temperature and unit cell numbers. For the Hall measurements, the magnetic field was applied along the surface plane.
and continuous way to tune the magnetic properties of freestanding membranes. The advantage of this cylinder diameter engineering strategy lies in the uniform uniaxial lattice deformation of quasi-2D crystals and is readily applicable to tune other intriguing physical properties.

3. Conclusions

We have fabricated the highly crystalline and stoichiometric Fe$_3$N single films and heterostructures using the plasma-assisted PLD technique. The intrinsic magnetic and electronic phase transitions at a critical thickness of $\approx 5$ u.c. were determined by the reduced dimensionality. The anomaly in the out-of-plane magnetic hysteresis loop was attributed to the reorientation of magnetic domains during field sweeping. Furthermore, we investigated the evolution of MR and AHE depending on the film thickness. The degeneracy in the in-plane magnetic responses and AHE signal reversal appeared as gradually increasing layer thickness. We attributed such behaviors to the band topology strongly associated with $k$-space Berry curvature, a typical character for ferromagnets with chiral spin texture. Finally, after field cooling to below the Néel temperature of CrN, a sizable in-plane exchange bias field of an AFM/FM heterointerface changed the sign. We demonstrated that the magnetic property of such a functional interface was highly tunable by modifying the diameter of the supporting sapphire cylinder in a large range. To this end, our work on manipulating the physical properties of high-quality nitride single films and all nitride heterostructures can be extended to various similar systems. Applying rare-earth-element-free nitrides with emergent magnetic properties will stimulate combination with other low-dimensional nanomaterials.

4. Experimental Section

Fabrication of High-Quality Samples: The Fe$_3$N thin films were fabricated by PLD assisted by radio-frequency plasma source supplying highly active nitrogen atoms. A stoichiometric ceramic Fe$_3$N target was synthesized using a high-pressure reaction route from a mixed FeCl$_3$ and NaNH$_2$ powder. The high-quality target fabrication was conducted at the High-Pressure Lab of South University of Science and Technology (SUSTech). This technique was used in a previous work and the details of fabrication process for the nitride bulk ceramics or single-crystals were described in previous works. The Fe$_3$N thin films were deposited at an optimized condition, that is, the substrate temperature of 400°C, laser density of $\approx 1$ J cm$^{-2}$, and base pressure of $1 \times 10^{-8}$ Torr. The films were grown under a nitrogen plasma. The high purity N$_2$ gas was activated into nitrogen atoms by a radio frequency plasma source with input power varied from 100 to 250 W and partial pressure of N$_2$ gas varied from $10^{-4}$ to $10^{-5}$ Torr. The plasma source was equipped with a parallel plate capacitor to remove ionic species within the plasma. The samples were cooled down to room-temperature under the irradiation of nitrogen plasma in order to compensate the NVs. The CrN/Fe$_3$N bilayer and superlattices were fabricated under the same experimental conditions. The layer thickness was carefully controlled by counting the number of laser pulses and further confirmed by X-ray reflectivity measurements. The number of bilayer repeats was kept the same for all superlattices in order to maintain the identical number of interfaces.

Manipulation of Bending Curvatures of Fe$_3$N/CrN Freestanding Membranes Using Cylinder Diameter Engineering: The Fe$_3$N/CrN bilayers...
were fabricated on the single-crystalline sodium chloride substrates under the same conditions. After the growth, the Fe₃N/CrN bilayers were immersed into the de-ionized water to dissolve the sodium chloride substrates. Then, the bilayers floated on the water surface. The sapphire cylinders with different curvatures (0, 0.1, and 0.25 mm) were used to scoop up the Fe₃N/CrN freestanding membranes. The membranes attached to the sticks firmly. The samples were hot dried in the oven at 100 °C for 2 h. The membranes suffered the bending stress from sapphire cylinders with different curvatures. This led to the lattice deformation and successful tuning of magnetic properties of membranes.

Physical Properties Characterizations: The crystallinity of samples was checked by in-house high-resolution four-circle XRD using a Cu Kα1 source (Parayntical MRD X’Pert 3). The microstructures of a Fe₃N single layer and a Fe₃N/CrN bilayer were examined using JEM ARM 200CF electron microscopy at the Institute of Physics, Chinese Academy of Sciences. Elemental-specific EELS mapping were performed at the Fe L-, Cr L-, N K-, and O K-edge from the interested regions after background subtracting. The magnetic properties of samples were characterized by a SQUID equipped with a high-temperature unit. Both in-plane and out-of-plane magnetization were obtained ranging from 10 to 500 K. The exchange bias was recorded at low temperatures after field-cooling down to 10 K under magnetic fields of ±3 T. The transport properties were performed using standard van der Pauw geometry with wire-bonding technique. The measurements were conducted using a 9T-PPMS. The AC current was kept at a minimum of 1 μA to avoid the Joule heating. XPS measurements were performed at the Institute of Physics, Chinese Academy of Sciences. Spectra were collected at both Fe 2p and N 1s core-level peaks at room-temperature.

Room-Temperature Magneto–Optical Kerr Effect Measurements: The MOKE measurements were performed using a commercial MOKE microscope from Evico Magnetics. The evolution of the magnetic domain structures was imaged and recorded using a quasi-static technique. The images were taken simultaneously by sweeping magnetic fields. Both in-plane and out-of-plane fields were applied during the imaging.

Polarized Neutron Reflectivity Measurements: The PNR experiments on the Fe₃N/CrN superlattices were performed at the BL-4A of Spallation Neutron Source, Oak Ridge National Laboratory. An in-plane magnetic field of 0.5 T was applied during the measurements. The two superlattices were measured simultaneously at room temperature to avoid any arbitrary effects. The PNR measurements on a Fe₃N/CrN bilayer were conducted with the multipurpose reflectometer at the Chinese Spallation Neutron Source. In this experiment, an in-plane magnetic field of 1 T was applied during the sample cooling. The measurements were conducted at the same magnetic field at 10 K. In both PNR measurements, the specular reflectivities were recorded as a function of the wave factor transfer along the film surface normal. R⁺ and R⁻ reflected the specular reflectivities from spin-up and spin-down polarized neutrons, respectively. The nuclear and magnetic scattering length densities were obtained simultaneously by fitting the PNR data using GenX software.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
cylinder diameter engineering, exchange bias, Fe₃N, magnetic anisotropy

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