

Erik Jonsson School of Engineering and Computer Science

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from Nitrogen Plasma Treatment of CoFeB Surfaces***

UT Dallas Author(s):

Eric C. Mattson
Jean Francois Veyan
Yves J. Chabal

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Cobalt and iron segregation and nitride formation from nitrogen plasma treatment of CoFeB surfaces

E. C. Mattson,¹ D. J. Michalak,² J. F. Veyan,¹ and Y. J. Chabal¹

¹Materials Science Department, University of Texas at Dallas, 600 W. Campbell Rd., Richardson, Texas 75080, USA

²Components Research, Intel Corporation, Hillsboro, Oregon 97124, USA

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Cobalt-iron-boron (CoFeB) thin films are the industry standard for ferromagnetic layers in magnetic tunnel junction devices and are closely related to the relevant surfaces of CoFe-based catalysts. Identifying and understanding the composition of their surfaces under relevant processing conditions is therefore critical. Here we report fundamental studies on the interaction of nitrogen plasma with CoFeB surfaces using infrared spectroscopy, x-ray photoemission spectroscopy, and low energy ion scattering. We find that, upon exposure to nitrogen plasma, clean CoFeB surfaces spontaneously reorganize to form an overlayer comprised of Fe₂N₃ and BN, with the Co atoms moved well below the surface through a chemically driven process. Subsequent annealing to 400 °C removes nitrogen, resulting in a Fe-rich termination of the surface region. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4964679>]

INTRODUCTION

The interactions between metal and semiconductor surfaces with nitrogen plasmas are important but complex and poorly understood reactions that have many important practical applications including steel hardening,¹ metal nitride growth² and deposition of anti-oxidation coatings or protective layers,³ and synthesis of biocompatible materials.⁴ Although there have been a number of investigations of plasma-nitrided materials,^{5–7} driven largely by interest in modifying the hardness and corrosion resistance of steels, the complex structures formed during initial surface nitridation have only recently begun to garner detailed attention,^{8–10} despite their critical role as device dimensions shrink.

For example, plasma nitridation of ferromagnetic thin films is an important potential route toward growth and modification of spintronic components,¹¹ in which ferromagnetic thin films are interfaced with insulating layers that serve as spin filters, or with metallic layers to form spin valves. CoFeB films are the industry standard for such magnetoresistive devices, with the highest tunneling magnetoresistance ratios reported for Ta/CoFeB/MgO multilayer structures¹² with stoichiometries optimized for Fe:Co ratios between 2.2 and 3.¹³ In the resulting heterostructures, the quality of the metal-oxide interface controls the performance of the device, as oxidation of the ferromagnetic electrode leads to impurities that can cause spin decoherence.¹⁴ Therefore, the optimization of practical spintronic devices in industry relies on the ability to prepare ferromagnetic surfaces with minimal oxidation, and also to chemically modify these surfaces to enable and optimize growth of spin filter layers. In addition, it may be useful to be able to tune the surface concentration of the components of the alloy to a value different than that of the bulk to optimize different aspects of device performance. For example, studies have shown that different

Fe:Co stoichiometries can have dramatic impacts on the value of the tunnel magnetoresistance,¹³ and the stoichiometry of magnetic binary alloys in general has also recently been shown to influence the rate of magnetic damping.¹⁵ Thus, the ability to tune the relative atomic concentrations of the surface relative to the bulk could provide an additional degree of freedom to tune device characteristics.

Since deposition of the magnet and tunnel barriers is a critical part of industrial processing, high volume manufacturing and even small lab engineering may require separate tools dedicated to each process separately (e.g., magnet deposition vs. tunnel barrier formation). To support transport of devices between tools, which typically requires an air break, we investigate the possibility of capping the CoFeB material with a temporary/protective nitride layer. Post annealing can remove this nitride layer, taking advantage of the low thermal stability of the nitrogen-rich phases of cobalt nitride¹⁶ and iron nitride.⁹ Additionally, the nonmagnetic properties of CoN and FeN¹⁷ make CoFeB surface nitridation a potential route toward incorporation of the nonmagnetic metallic layer of spin valve structures. However, in order to explore the potential of these approaches, a method by which to obtain a well-defined surface nitride layer must be realized.

Surface nitridation with a nitrogen plasma is one appealing route, as this can yield a thin, sometimes stoichiometric nitride^{10,18} with minimal oxidation in a single processing step. Nitridation of CoFe alloys is also interesting because, as these alloys and their oxides are commonly employed catalyst materials in a wide variety of reactions including solar-driven hydrogen evolution, Fisher-Tropsch reactions, and methane decomposition,^{19–23} and the catalytic activity of Co and Fe nitrides toward reactions including oxygen evolution, hydrazine decomposition, Fisher-Tropsch reactions, and others has become apparent as well.^{24–28}

Plasma nitridation of pure Fe or Co has been previously reported;^{18,29} however, nitridation of a CoFe alloy containing B is more complex and needs detailed experiments to unravel the fundamental chemistry involved in the surface region evolution.

To this end, we have studied the interaction of a nitrogen remote plasma with CoFeB surfaces in a special ultrahigh vacuum (UHV) cluster tool comprising IR spectroscopy, x-ray photoemission spectroscopy (XPS), and low energy ion scattering spectroscopy (LEIS). Surprisingly, we find that both B and Fe are highly reactive toward nitrogen plasma and form respective nitrides, i.e., the formation of a Co nitride appears thermodynamically unfavorable relative to the formation of a Fe and B nitride, leading Co atoms to segregate below the surface region comprised of Fe₂N₃ and BN. This result is interesting because we know from previous work²⁹ that the formation of CoN from clean cobalt surfaces is possible in the same plasma system. This surface layer can be decomposed by annealing to 400 °C, leading to an iron-rich surface termination with low levels of residual nitrogen. The fundamental understanding of surface chemistry derived from this work provides a platform for engineering spintronic interfaces and catalytic materials.

EXPERIMENTAL METHODS

All measurements described here were carried out using an ultra-high vacuum (UHV) cluster system combining chambers for remote plasma treatment and *in situ* grazing incidence IR reflectance measurements, XPS, and LEIS, with two connecting chambers for UHV sample transfer. The base pressure of the cluster system was $<4 \times 10^{-10}$ Torr. IR reflectance measurements were performed at grazing incidence (80° with respect to the sample normal) using a Thermo FTIR spectrometer. The spectra were generated from 1500 co-added scans with a spectral resolution of 4 cm⁻¹. All IR measurements and plasma exposures were performed with the sample maintained at 50 °C. X-ray photoemission spectroscopy (XPS) measurements were carried out using a Physical Electronics Quantum 2000 ESCA Microprobe equipped with a hemispherical analyzer, an AlK_α radiation source, and a detection takeoff angle of 45°. The pass energy used was 187 eV for survey spectra and 11.75 eV for high-resolution spectra of individual core levels. Low energy ion scattering (LEIS) measurements were performed in a UHV chamber equipped with an IonTOF Qtac¹⁰⁰ ion detector, using either 3 keV He⁺ or 5 keV Ne⁺ as the probe ions.

Stacks comprised of 30 nm Co_{0.25}Fe_{0.5}B_{0.25}/30 nm Ta/100 nm SiO₂ films on a 500 μm-thick Si substrate were prepared by DC magnetron sputtering in a separate tool with a base pressure of $<10^{-8}$ Torr. The 100 nm SiO₂ layer was grown by thermal oxidation of lightly doped (5–25 Ω-cm) p-type Si(100) wafers. The CoFeB stoichiometry, multilayer structure, and film thicknesses were grown to conform to the industry standard for CoFeB/MgO-based spintronic devices; the parameters were therefore selected such that the fundamental studies performed here emulate the

characteristics of actual devices. After deposition, the surfaces were transported to our UHV cluster analysis system and were prepared under UHV by annealing to 400 °C, followed by 3 keV Ar⁺ ion sputtering at 45° with respect to the sample normal. The most sensitive measure of surface cleanliness was obtained by LEIS measurements of the O signal intensity. When all surface impurities were removed, the LEIS O signal ceased to decrease, as described below. The plasma nitridation was performed using an inductively coupled radiofrequency (RF, 13.56 MHz) remote plasma-source (SPECS PCS-RF) operating at an incident power of 175 W and a high purity N₂ source (99.999% purity, Airgas). During operation, the chamber pressure was 3×10^{-5} Torr, and the plasma source provided a flux of $\approx 10^3$ atoms/(cm²/s), with an ion energy of ~ 25 eV. The plasma source is mounted on the IR chamber of the UHV cluster, approximately 38 cm from the sample in the IR measurement position. Plasma treatments were performed until the IR signal did not change any longer, typically ≈ 15 –20 min in the geometry used here. The substrate temperature was selected to be 50 °C to enable direct comparison to existing work on nitridation of pure Co²⁹ and Fe¹⁸ systems, and to stay safely below the 200 °C decomposition temperature of CoN.¹⁶

Pure Co and Fe films (Alfa Aesar, 99.9% pure) cleaned by Ar⁺ sputtering were used to calibrate the binding energies in the Fe2p and Co2p regions.

RESULTS

XPS is the best technique to determine the chemical bonding of metal atoms in metallic films and was used first to characterize the CoFeB samples. Figures 1(a)–1(e) compare XP spectra of a CoFeB film following cleaning by annealing and sputtering and after 15 min exposure to the nitrogen plasma. Fig. 1(f) compares the Co2p and Fe2p core levels in CoFeB with pure Co and Fe reference samples. We first note several important features observed in the cleaned surfaces: first, there is a small amount of residual oxygen (Fig. 1(c)) that remains despite prolonged sputtering. We routinely observed this effect, which could arise due to small levels of oxygen impurities throughout the depth of the film, from intermixing resulting from the long sputtering treatments, or from trace quantities of boron oxide that forms following annealing due to reaction with the native oxide. In addition, comparison of the Fe2p and Co2p levels in CoFeB and the respective pure standards shows that both levels in CoFeB are shifted by ≈ 0.1 eV to lower binding energy from their position in the pure standards. We also note that, while the unannealed, sputter-cleaned surfaces show the nominal Co_{0.25}Fe_{0.5}B_{0.25} stoichiometry as determined by XPS, the surfaces cleaned by annealing followed by sputtering show a Co_{0.33}Fe_{0.61}B_{0.06} stoichiometry. The most significant compositional difference in the samples cleaned by annealing followed by sputtering is the deficiency of B relative to its concentration in the as-grown material. This occurs for the following reason: following annealing, a reaction between B atoms and the native oxide on the CoFeB surface takes place. Previous work has shown that in the temperature range considered, B atoms diffuse to

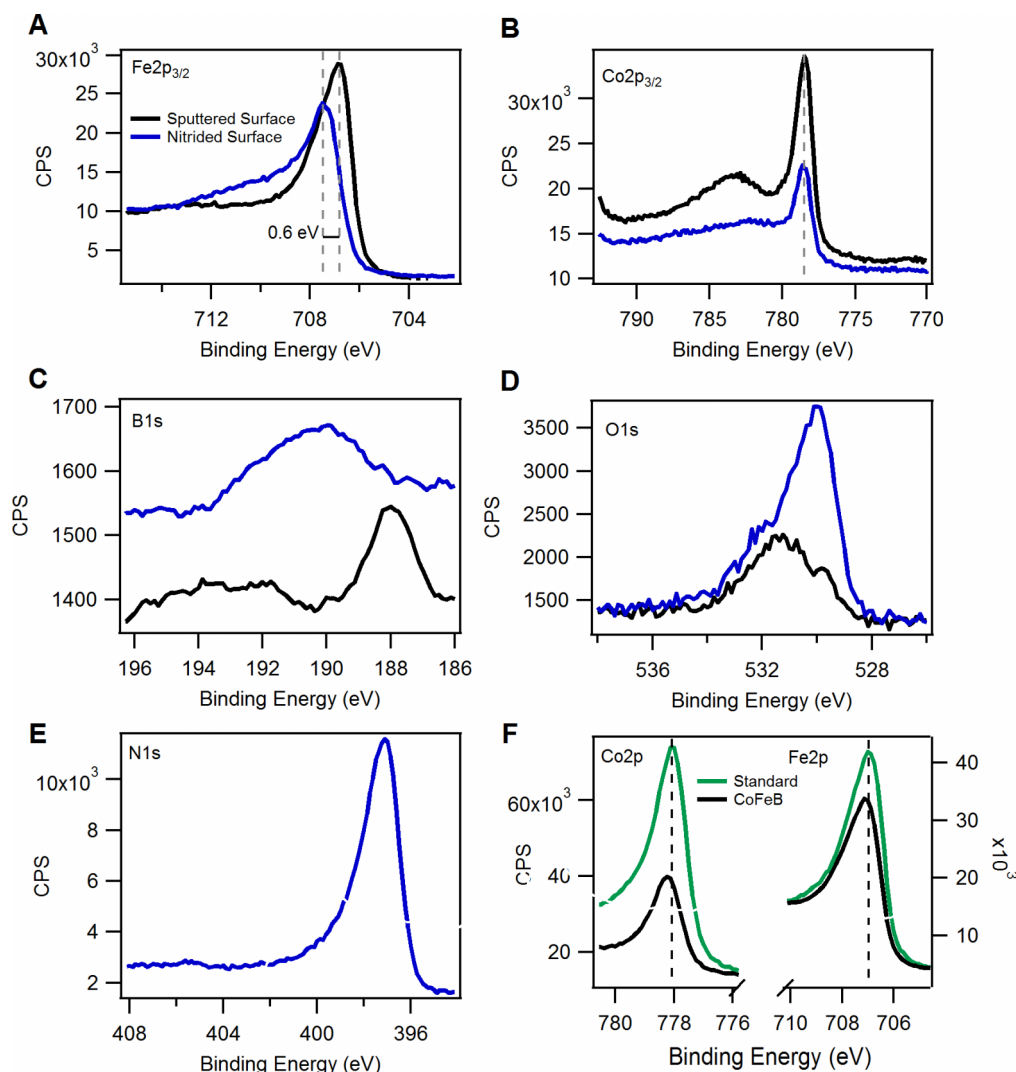


FIG. 1. XPS spectra of clean and nitrided CoFeB films. (a) Fe_{2p_{3/2}} spectrum shows 0.6 eV chemical shift following nitrogen plasma treatment. (b) The Co_{2p_{3/2}} spectrum shows significantly reduced intensity but no chemical shift following nitrogen plasma treatment. (c) B_{1s} shows increase in intensity and shift to higher binding energy following nitridation. (d) O_{1s} shows increase in components due to metal oxide and NO⁺ following plasma treatment. (e) N_{1s} spectrum shows the presence of nitrogen following plasma treatment. (f) Comparison of Fe_{2p} and Co_{2p} edges in CoFeB with those in pure Co and Fe standard samples.

the surface and reduce the Co and Fe atoms at the surface, forming a boron oxide layer.³⁰ As a result of this reaction, there is an accumulation of the B atoms at the surface forming a boron oxide layer. This layer is preferentially removed by the subsequent Ar⁺ sputtering treatment, exposing the underlying CoFeB film, which is comparatively B-deficient as a result of the pretreatment. We verified that similar results are observed, namely the preferential segregation of Co and Fe and gettering of Fe to the surface, in samples that were prepared only by sputtering.

Several prominent differences are observed in all of the core levels measured following exposure to nitrogen plasma. In the Fe_{2p_{3/2}} spectrum (Fig. 1(a)), a slight decrease in intensity is accompanied by a chemical shift of 0.6 eV toward higher binding energy relative to its position in clean CoFeB. In contrast, the Co_{2p_{3/2}} spectrum (Fig. 1(b)) demonstrates no appreciable chemical shift, yet shows a dramatic reduction in overall intensity. We have previously measured a shift of -0.4 eV due to CoN formation for pure Co films exposed to the same nitrogen plasma, so

the lack of a shift implies no CoN formation within the escape depth of the XPS measurement. The O_{1s} spectrum shows an increase in the components due to metal oxide (530 eV) and NO⁺ (≈530.7 eV), which is consistent with earlier studies²⁹ showing that plasma nitridation results in incorporation of oxygen leading to adsorbed NO⁺ and trace metal oxide, which most likely originates from the SiO₂ tube of the plasma source. The B_{1s} spectrum of the clean surface is observed at the position expected for metallic B, indicating its form is the predominantly dissolved B in the film. Following exposure to nitrogen plasma, the peak appears broadened and with significantly higher intensity (integrated area) than that of the clean surface, and also shows a chemical shift toward higher binding energy. We note that there is some signal in the 192-196 eV region of the sputtered surface, indicating that a small amount of residual boron oxide remained following sputtering. The chemical shift for the majority of the signal of the B_{1s} spectrum from the plasma-treated surface is consistent with the presence of BN; however, some of the intensity from

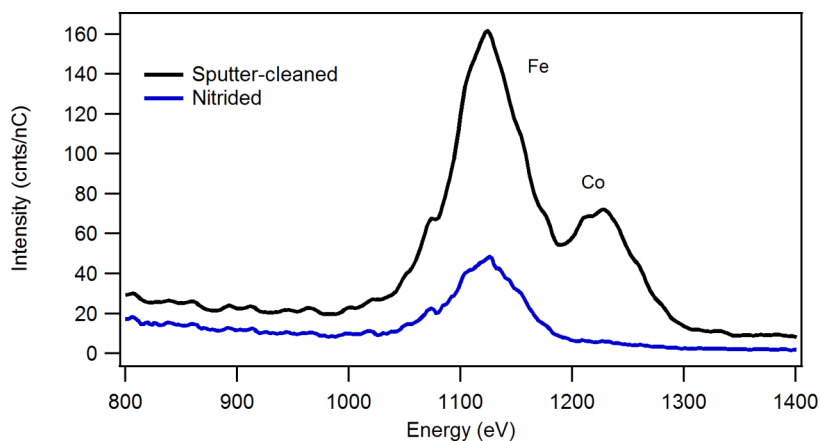


FIG. 2. Ne^+ LEIS spectra of sputter-cleaned and nitrided CoFeB surfaces. The data show the presence of both Fe and Co on the clean surface, but only Fe following nitrogen plasma treatment.

the high binding-energy end of the peak could arise from boron oxynitride, likely originating from the small amount of residual boron oxide and/or minority oxygen impurities introduced from the plasma source. Stoichiometric boron oxide is ruled out, however, based on measurements of boron oxide (produced by annealing to 400 °C, sufficient to form pure boron oxide) characterized by a binding energy of 196 eV. Similarly, measurements of the B1s spectra of the as-received samples (i.e., with a native oxide) showed a peak at 194 eV corresponding to substoichiometric boron oxide. Thus, both measurements of boron oxide show binding energies considerably higher than that observed following nitrogen plasma treatment (190–193 eV), which points to a mixture of BN and boron oxynitride in the plasma-treated samples. These data suggest that the nitrogen plasma reacts preferentially with Fe and B over Co, resulting in iron nitride and boron nitride phases at the outermost surface.

LEIS is best to identify species at the outermost surface and ideal to understand the structural evolution and reactivity of the films subjected to plasma treatment. Fig. 2 shows LEIS spectra of the clean and nitrogen plasma-treated surfaces collected with 5 keV Ne^+ , which is sufficient to resolve Fe and Co that have close masses (56 and 59 amu). The spectrum of the clean surface shows two peaks at the positions expected for Fe and Co, whereas the spectrum of the plasma-treated surface only shows one peak associated with Fe. These data indicate that only Fe atoms are present at the surface, and Co has been driven below the surface. In conjunction with the XPS data

presented above, these data suggest that the nitrogen plasma has the effect of segregating Fe and Co by preferentially reacting with Fe over Co, resulting in a chemically induced diffusion process.

Further insight into the interaction of the nitrogen plasma with the CoFeB surfaces is obtained by IR reflectance measurements collected *in situ* upon nitrogen plasma treatment. Figure 3 shows the reflectivity of the CoFeB surfaces following 15 min exposure to nitrogen plasma, referenced to that of the clean surface immediately before exposure. In this geometry, the appearance of absorption bands is a negative feature in the reflectance spectrum. Several chemically distinct modes are present: first, a negative feature at 2190 cm^{-1} is attributed to adsorbed NO^+ , which has been shown to be a byproduct of the plasma processing for several other metal nitride systems.^{8,29} In the case of nitridation of pure Co, a feature of very similar intensity was observed at 2187 cm^{-1} ; based on the close proximity of the modes observed for NO^+ on pure Co and on CoFeB, we can conclude that the NO^+ is adsorbed at a metal site, rather than an N-top site. Furthermore, if the NO^+ were coordinated to another N atom incorporated into the nitride structure to form an N_2O^+ complex, the corresponding modes would have $\text{N}=\text{O}$ stretching frequencies much lower (<1400 cm^{-1})³¹ than those observed here. Furthermore, given the absence of Co present at the surface as indicated by the LEIS spectra in Fig. 2, we can conclude that the NO^+ is coordinated to Fe. Second, two modes of similar intensity are observed in the low-frequency

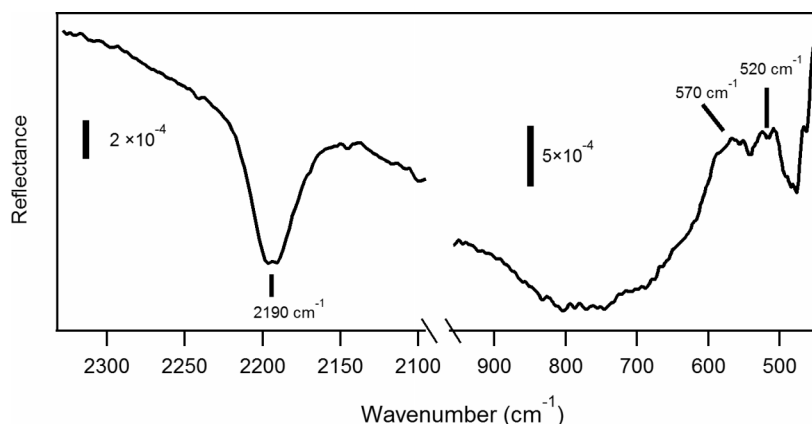


FIG. 3. IR reflectance measurements taken following nitrogen plasma treatment referenced to the reflectance of the clean surface immediately before plasma exposure.

region, but are observed as positive bands. Although such bands could be due to the loss or reaction of chemical bonds originally on the reference surface, this is unlikely because the reference surface is chemically clean; i.e., the remaining bonds on the surface are Co–Fe, Co–B/Fe–B, and minority BO_x , none of which are expected to produce measurable bands in the region under consideration. Interestingly, we previously observed a similar band inversion effect in the spectra of nitrogen plasma-treated Co films, and found that the origin of the effect was related to an intense electronic absorption in the same energy range due to internal d - d excitations arising from spin-orbit splitting of degenerate d -levels.³² Specifically, we concluded on the basis of a series of optical simulations that the presence of an adlayer with an intense, strongly dispersing absorption band caused a modification of the modes in that layer such that the modes in that spectral region demonstrated derivative-like lineshapes, with both positive and negative contributions.²⁹ Here, we observe a similar broadband absorption feature in the spectra from this system and therefore attribute the two modes at 520 and 570 cm^{-1} to bonds formed upon N plasma treatment. Although the frequency at which the negative contribution of the bands would be expected is nearly at the spectral limit of the detector, the spectrum is decreasing with wavenumber until the detector limit is reached, consistent with the behavior expected on the basis of the optical simulations discussed above.

DISCUSSION

The results in Figs. 1 and 2 demonstrate unambiguously that, following exposure to nitrogen plasma, clean CoFeB surfaces undergo chemical reactions that result in diffusion of Co below an iron nitride overlayer that also contains boron nitride and minority Fe oxynitride. In the sections titled “Deconvolution of core-level spectra of nitrified CoFeB and estimation of overlayer thickness” and “Nitride overlayer composition,” we attempt to further clarify the chemical structure of the resulting nitride overlayer. We first deconvolve the measured core-level spectra to identify distinct chemical components present in the structure. We then evaluate the overlayer thickness and quantify the stoichiometry of the

nitride layer. Lastly, we show that the segregation of Co and Fe induced by the nitrogen plasma can in principle be used to tune the Fe content present at the surface of CoFeB films.

Deconvolution of core-level spectra of nitrified CoFeB and estimation of overlayer thickness

We perform the deconvolution of the $\text{Fe}2p$ and $\text{N}1s$ core-level spectra of the plasma-treated CoFeB surfaces to quantify the type and amount of chemical bonds present, as shown in Figs. 4(a) and 4(b). Four peaks are used to fit the $\text{Fe}2p_{3/2}$ spectrum, denoted I, II, III, and IV in Fig. 4(a). The parameters used for fitting these peaks as well as the four peaks used for deconvolution of the $\text{N}1s$ (discussed below) are summarized in Table I. The peak denoted I is due to the majority iron nitride species, and its peak position is shifted by +0.57 eV from that of the $\text{Fe}2p_{3/2}$ peak in clean CoFeB. The peak denoted II describes the contribution of the remaining metallic Fe, which resides below the iron nitride and therefore is heavily attenuated. The peaks denoted III and IV are due to oxide satellites that arise due to the incorporation of oxygen in the plasma processing, and their position and width are consistent with values used previously to describe the deconvolution of the $\text{Fe}2p$ spectrum.³³ We note that the total integrated area of these peaks is consistent with the integrated area of the metal oxide component of the $\text{O}1s$ spectrum following plasma treatment. Specifically, when the integrated area of the satellites III and IV is scaled by the appropriate sensitivity factors, the corresponding intensity that would be expected for the $\text{O}1s$ line is within 6% of the measured intensity of the metal oxide component (530.0 eV) of the $\text{O}1s$ in Fig. 1(d). Thus, the data are consistent and confirm that the inclusion of these peaks is appropriate and quantitatively reasonable.

The $\text{N}1s$ spectrum is deconvolved into four peaks denoted V, VI, VII, and VIII in Fig. 4(b), similar to the approach used previously for quantification of cobalt nitride.²⁹ Peak V is representative of adsorbed NO^+ , and is similar in magnitude to that observed previously for NO^+ on cobalt nitride. The binding energy of peak VI is coincident with boron nitride binding energies, as verified by measurements of the binding energy in the $\text{N}1s$ spectrum of boron nitride of a reference

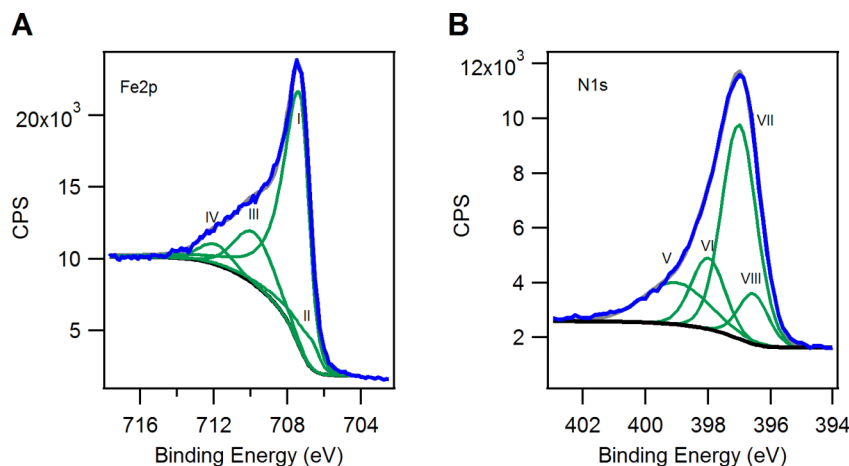


FIG. 4. Deconvolution of $\text{Fe}2p_{3/2}$ (a) and $\text{N}1s$ (b) XPS spectra. The components marked I, II, III, and IV in (a) are assigned, respectively, to iron nitride, metallic iron, and two oxide satellites. Those marked V, VI, VII, and VIII in (b) are assigned, respectively, to NO^+ , iron oxynitride, and boron nitride (overlapping), iron nitride, and surface shifted iron nitride.

TABLE I. Parameters used for fitting the Fe2p and N1s spectra in Fig. 4 and their assignments.

Peak	FWHM (eV)	Position (eV)	Area (eV·CPS)	Assignment
I	1.19	707.3	37995	Iron nitride
II	1.07	706.7	4773	Metallic iron
III	2.57	709.8	10205	Iron oxynitride
IV	2.59	712.0	4278	Iron oxynitride
V	2.30	399.0	4056	NO+
VI	1.30	397.9	4242	BN, iron oxynitride
VII	1.25	397.0	10232	Iron nitride
VIII	1.14	396.5	2311	Iron nitride surface shift

sample performed on the same instrument, and also metal oxynitride, as inferred from analogous measurements on nitrified cobalt.²⁹ Peak VII is representative of Fe nitride, and peak VIII is representative of the surface shifted iron nitride, i.e., the undercoordinated N atoms at the surface. The shift of peak VIII relative to the “bulk” nitride peak (VII), 0.5 eV, is typical for transition metal nitrides,^{34,35} and on par with that reported for nitridation of an Fe(100) single crystal.¹⁸

The thickness of the overlayer on a substrate can be estimated from an XPS spectrum by considering the attenuation of the substrate,

$$I = I_0 e^{-d/\lambda \cos \theta}, \quad (1)$$

where I is the intensity of the substrate core level in the presence of the overlayer, I_0 the intensity of the substrate core level in the absence of the overlayer, d is the thickness of the overlayer, θ is the takeoff angle of photoemitted electrons, and λ is the inelastic mean free path (IMFP) of an electron in the overlayer material at the kinetic energy corresponding to a given core level and x-ray energy. In the system at hand, the situation is complicated by the fact that the surface reaction induced by the plasma processing inherently changes the composition of the substrate: following plasma exposure, there is evidence for preferential diffusion of Co atoms away from the surface, which likely results in a gradient below the overlayer that is both Co-rich and Fe-poor relative to the composition of the clean substrate. Consequently, quantification with Equation (1) using the metallic Co2p and Fe2p peaks of the clean and nitrified surfaces provides upper and lower bounds on the overlayer thickness, respectively. We estimate the IMFP of the nitride overlayer using the TTP-2M equation as implemented in the NIST IMFP database (SRD 71) by assuming a Fe₂N₃ stoichiometry, as summarized in Table II and discussed below. We then estimate the thickness using the measured intensities of the metallic Fe2p_{3/2} and Co2p_{3/2} core level peaks from the clean and plasma-treated surfaces. Using these values in Equation (1), we obtain 1.0 nm and 2.9 nm for the overlayer thickness when estimated from the Fe2p_{3/2} and Co2p_{3/2} levels, respectively. As stated above, the discrepancies in these values arise due to the Co-rich, Fe-poor region that forms the following plasma treatment, and therefore these values should be treated as upper and lower bounds on the actual value of the thickness estimate.

TABLE II. Inelastic mean free path of Fe₂N₃ for photoelectrons with kinetic energies corresponding to emission from different core levels.

Core-level	λ (nm)
Co2p _{3/2}	1.50
Fe2p _{3/2}	1.61
O1s	1.88
N1s	2.07
B1s	2.35

Nitride overlayer composition

The deconvolution of the core-levels in Figure 4 can be used to estimate the stoichiometry of the iron nitride layer formed following nitrogen plasma treatment; however, due to the different IMFPs care must be taken in the quantification to avoid error associated with the finite sample thickness. Specifically, a photoelectron emitted from the N1s level has a larger kinetic energy and therefore longer IMFP than the one emitted from the Fe2p level; consequently, the Fe2p photoelectrons will suffer more scattering events than the N1s electrons, leading to the preferential detection of N. For thin films and short IMFPs, this effect becomes increasingly significant with decreasing thickness and leads to additional errors in the estimate of the stoichiometry. We detail below the method used to account for this effect. The relative sensitivity factor (RSF) developed by Wagner³⁶ considers the photoemission intensity originating from a semi-infinite film, such that

$$I_\infty = k \int_0^\infty \exp\left(-\frac{x}{\lambda \cos \theta}\right) dx = k \lambda \cos \theta, \quad (2)$$

where x is the distance into the surface and k is a constant determined by the photoelectric cross-section, atom density, detection efficiency, angular collection efficiency, illuminated sample area, and x-ray flux. In the case of a thin film, the analogous photoelectron yield is

$$I = k \int_0^d \exp\left(-\frac{x}{\lambda \cos \theta}\right) dx = k \lambda \cos \theta \left(1 - \exp\left(-\frac{d}{\lambda \cos \theta}\right)\right) \quad (3)$$

so that

$$\frac{I_\infty}{I} = \frac{1}{1 - \exp\left(-\frac{d}{\lambda \cos \theta}\right)}. \quad (4)$$

In the case of a thin film with core levels A and B, the different values of λ originating from the fact that electrons emitted from different core levels have different kinetic energy will lead to different values of $\frac{I_\infty}{I}$, and consequently the stoichiometry obtained by taking the ratio of the photoemission intensity from the levels A and B with their respective RSFs will be off by a factor of

$$c = \frac{1 - \exp\left(-\frac{d}{\lambda_A \cos \theta}\right)}{1 - \exp\left(-\frac{d}{\lambda_B \cos \theta}\right)}. \quad (5)$$

Therefore, in evaluating the stoichiometry of the iron nitride from our data, we scale the data by the value of the constant factor c in Eq. (5). If we assume a 2 nm

thick film and use the IMFP values given in Table II for the N1s and Fe2p core levels, the constant in Eq. (5) is equal to 1.1. Thus, to evaluate the Fe:N ratio of the iron nitride, we compute the area ratio of the peaks denoted I and VII in Figs. 4(a) and 4(b), scaled by the appropriate relative sensitivity factors, and divide by 1.1 to account for the preferential sensitivity toward N due to the longer IMFP. The resulting Fe:N ratio obtained by this procedure is 0.64, which is reasonably close to the value of 0.67 expected for an ideal Fe_2N_3 . The deviation from the ideal stoichiometry is not surprising given the presence of extrinsic oxygen and the approximations used for performing the overlayer thickness calculations, peak deconvolution, and stoichiometry estimates.

The observation of such a low Fe:N ratio is interesting in light of previous studies on transition metal plasma nitridation. Navío *et al.*¹⁸ reported on the interaction of nitrogen plasma with a pure bcc Fe(100) single crystal, identifying an FeN phase through a combination of photoemission and x-ray diffraction measurements. They deconvolved the $\text{Fe}2p_{3/2}$ core-level measured from photoemission measurements to obtain the stoichiometry in a fashion very similar to that reported here. In their data, the Fe2p spectrum of the FeN showed a chemical shift of 0.36 eV toward higher binding energy with respect to pure Fe. The Fe2p chemical shift of the nitrated CoFeB surface measured in our data (0.6 eV) is considerably larger than the 0.36 eV value reported by Navío *et al.*¹⁸ and the 0.4 eV shift reported for nitridation of pure Co to form CoN, thus consistent with the iron nitride layer formed here being considerably more nitrogen rich than FeN.

The B1s binding energy following plasma exposure is consistent with that expected for BN, as verified from a reference BN sample measured on the same instrument.

We also evaluate the amount of B present in the nitride overlayer using the approach detailed above for the Fe:N ratio, and find a Fe:B ratio of 4.6. Thus, assuming that the nitride overlayer is comprised of a heterogeneous mixture of Fe_2N_3 and BN, its composition is 22% BN and 78% Fe_2N_3 .

We further note that the assignment of the iron nitride to Fe_2N_3 is also supported by the IR data. In the IR spectrum in Fig. 3, we observe two distinct modes in the 500-600 cm^{-1} region, where the Fe-N stretching modes of iron nitride are expected. Some insight into the structures giving rise to these modes can be obtained by considering the isostructural iron oxide analogues. In particular, the compound wüstite (FeO) possesses rock-salt structure, and therefore has one infrared active mode corresponding to Fe-O stretching.^{37,38} The compound maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is cubic and crystallographically similar to the spinel structure, and has four IR active modes.³⁹ Of these four modes, the one of the two IR active T_{1u} modes corresponding to Fe-O stretching is centered around 550-570 cm^{-1} and is split due to vacancy ordering. As a result, two prominent modes of comparable intensity are commonly observed at 560 and 620 cm^{-1} , with additional weaker shoulders present to varying degrees dependent on the sample geometry and degree of vacancy ordering. These frequencies and the splitting between them are similar to the frequencies we observed (520 and 570 cm^{-1}), and the slightly lower values we observe are likely due to the fact that iron nitrides, unlike most iron oxides, are metallic. Additionally, some isolated iron nitride molecules have been shown to have lower vibrational frequencies than isostructural iron oxide molecules, despite being lower in mass. Thus, given the known modes of the iron oxides, the number and spacing of vibrational modes of iron nitride presented here most closely correspond to the nitride analog

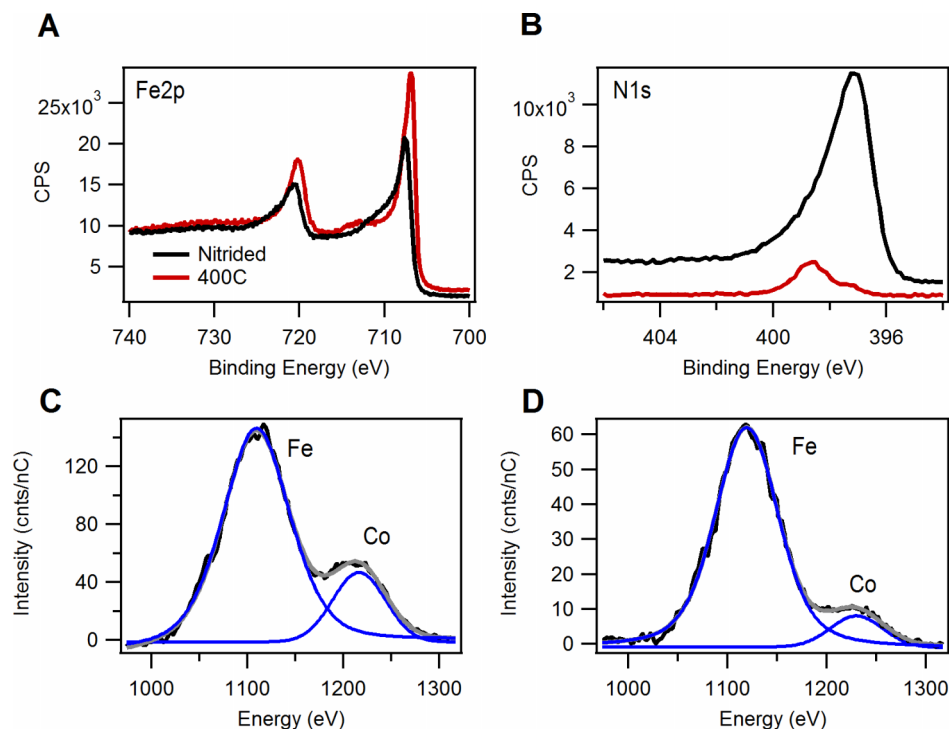


FIG. 5. (a) Fe2p and (b) N1s spectra of CoFeB as-nitrided and upon annealing to 400 °C. LEIS spectra from (c) clean CoFeB surfaces and (d) CoFeB surfaces exposed to nitrogen plasma and subsequently annealed to 400 °C are deconvoluted into components due to Fe and Co.

of Fe₂O₃, consistent with the XPS and FTIR data discussed above.

Evolution of surface composition upon annealing

The ability of nitrogen plasma to preferentially getter Fe atoms in CoFeB films has interesting implications for tailoring the surface composition of CoFe films. In particular, the low decomposition temperature for Fe and Co nitrides suggests some degree of reversibility in the nitridation process. Figs. 5(a) and 5(b) show the evolution of the Fe2p and N1s core-level spectra of CoFeB surfaces treated by a nitrogen plasma upon annealing to 400 °C. We chose 400 °C as the annealing temperature as it is sufficient to decompose FeN, CoN, and cobalt oxynitride and to enable diffusion of Co and Fe, but not so high as to enable in-diffusion of Ta,¹³ and showed that most of the nitrogen is removed from the film. Indeed, the Fe2p core-level shift observed on the nitrided surface (Fig. 1) vanishes, i.e., its position reverts to that in clean CoFeB. The LEIS measurements on the films annealed to 400 °C and compared the spectra to those of the clean CoFeB surface of the same sample (prepared prior to exposure to nitrogen plasma), shown in Figs. 5(c) and 5(d), and make it possible to quantify the surface composition. By deconvolving the spectra in the 1050–1250 eV region into components due to Fe and Co, the change in the relative intensities of the Co and Fe peaks is measured, showing a much smaller Co component in the sample treated with nitrogen plasma and subsequent annealing. The presence of Co at the surface following annealing is not surprising given that Co and Fe atoms in CoFeB become mobile and ultimately crystallize at 380 °C.⁴⁰ The Co:Fe peak area ratio decreases from 0.25 in the case of the clean surface (Fig. 5(c)) to 0.12 in the nitrided and annealed surface (Fig. 5(d)), indicating that the combined processes lead to a doubling of the surface Fe concentration. Thus, these results suggest that annealing after plasma nitridation can be used to tune the concentration of surface Fe:Co atoms. Further investigation is needed to detail the relationships between surface concentration with annealing time and temperature, and potentially repeated plasma/annealing cycles.

CONCLUSIONS

This spectroscopic study of CoFeB surfaces prepared by 400 °C annealing and sputtering reveals that the clean surface contains both Fe and Co in a ≈4:1 ratio. Exposure of clean CoFeB surfaces to a remote nitrogen plasma leads to a restructuring of the near surface region, gettering Fe and B atoms to the surface to form a mixed iron nitride/boron nitride overlayer, and thereby migration of Co atoms into the bulk with no detectable chemical shift. The estimated stoichiometry, Fe2p chemical shift, and number and frequency of measured IR bands are all consistent with Fe₂N₃ stoichiometry in the iron nitride phase. The overlayer thickness, though difficult to estimate, is between 1 and 3 nm. Most of the nitrogen in the system can be removed by annealing to 400 °C, and

the resulting surface composition is Fe-rich, with an Fe concentration over twice that of the clean surface. These results have important implications for spintronics and catalysis applications, as they suggest a novel approach for tailoring the surface composition of CoFe alloys and a method for growth of Fe₂N₃ films.

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- ¹E. Menthe, A. Bulak, J. Olfe, A. Zimmermann, and K. T. Rie, "Improvement of the mechanical properties of austenitic stainless steel after plasma nitriding," *Surf. Coat. Technol.* **133–134**, 259–263 (2000).
- ²O. Ambacher, "Growth and applications of group III nitrides," *J. Phys. D: Appl. Phys.* **31**(20), 2653–2710 (1998).
- ³A. L. Yerokhin, X. Nie, A. Leyland, A. Matthews, and S. J. Dowey, "Plasma electrolysis for surface engineering," *Surf. Coat. Technol.* **122**(2–3), 73–93 (1999).
- ⁴K. Bordji, J. Y. Jouzeau, D. Mainard, E. Payan, P. Netter, K. T. Rie, T. Stucky, and M. Hage-Ali, "Cytocompatibility of Ti-6Al-4V and Ti-5Al-2.5Fe alloys according to three surface treatments, using human fibroblasts and osteoblasts," *Biomaterials* **17**(9), 929–940 (1996).
- ⁵I. Bertoti, M. Mohai, J. L. Sullivan, and S. O. Saied, "Surface characterization of plasma-nitrided titanium - an XPS study," *Appl. Surf. Sci.* **84**(4), 357–371 (1995).
- ⁶E. Menthe, K. T. Rie, J. W. Schultze, and S. Simson, "Structure and properties of plasma-nitrided stainless-steel," *Surf. Coat. Technol.* **74–75**(1–3), 412–416 (1995).
- ⁷B. Larisch, U. Brusky, and H. J. Spies, "Plasma nitriding of stainless steels at low temperatures," *Surf. Coat. Technol.* **116**, 205–211 (1999).
- ⁸S. Sato, K. Omori, S. Araki, Y. Takahashi, and K. Wagatsuma, "Surface analysis of nitride layers formed on Fe-based alloys through plasma nitride process," *Surf. Interface Anal.* **41**(6), 496–501 (2009).
- ⁹C. Navio, J. Alvarez, M. J. Capitan, F. Yndurain, and R. Miranda, "Nonmagnetic γ'-FeN thin films epitaxially grown on Cu(001): Electronic structure and thermal stability," *Phys. Rev. B* **78**(15), 155417 (2008).
- ¹⁰H. M. Lee, C. T. Kuo, H. W. Shiu, C. H. Chen, and S. Gwo, "Valence band offset and interface stoichiometry at epitaxial Si₃N₄/Si(111) heterojunctions formed by plasma nitridation," *Appl. Phys. Lett.* **95**(22), 222104 (2009).
- ¹¹I. Žutić, J. Fabian, and S. Das Sarma, "Spintronics: Fundamentals and applications," *Rev. Mod. Phys.* **76**(2), 323–410 (2004).
- ¹²S. Ikeda, K. Miura, H. Yamamoto, K. Mizunuma, H. D. Gan, M. Endo, S. Kanai, J. Hayakawa, F. Matsukura, and H. Ohno, "A perpendicular-anisotropy CoFeB-MgO magnetic tunnel junction," *Nat. Mater.* **9**(9), 721–724 (2010).
- ¹³S. Ikeda, J. Hayakawa, Y. Ashizawa, Y. M. Lee, K. Miura, H. Hasegawa, M. Tsunoda, F. Matsukura, and H. Ohno, "Tunnel magnetoresistance of 604% at 300 K by suppression of Ta diffusion in CoFeB/MgO/CoFeB pseudo-spin-valves annealed at high temperature," *Appl. Phys. Lett.* **93**(8), 082508 (2008).
- ¹⁴A. Vedyayev, D. Bagrets, A. Bagrets, and B. Dieny, "Resonant spin-dependent tunneling in spin-valve junctions in the presence of paramagnetic impurities," *Phys. Rev. B* **63**(6), 064429 (2001).
- ¹⁵M. A. W. Schoen, D. Thonig, M. L. Schneider, T. J. Silva, H. T. Nembach, O. Eriksson, O. Karis, and J. M. Shaw, "Ultra-low magnetic damping of a metallic ferromagnet," *Nat. Phys.* **12**(9), 839–842 (2016).
- ¹⁶K. Suzuki, T. Kaneko, H. Yoshida, H. Morita, and H. Fujimori, "Crystal structure and magnetic properties of the compound CoN," *J. Alloys Compd.* **224**(2), 232–236 (1995).
- ¹⁷P. Lukashev and W. R. L. Lambrecht, "First-principles study of the preference for zinc-blende or rocksalt structures in FeN and CoN," *Phys. Rev. B* **70**(24), 245205 (2004).
- ¹⁸C. Navío, M. J. Capitan, J. Alvarez, R. Miranda, and F. Yndurain, "Formation of a non-magnetic metallic iron nitride layer on bcc Fe(100)," *New J. Phys.* **12**(7), 073004 (2010).
- ¹⁹V. R. Calderone, N. R. Shiju, D. C. Ferre, and G. Rothenberg, "Bimetallic catalysts for the fischer-tropsch reaction," *Green Chem.* **13**(8), 1950–1959 (2011).

- ²⁰M. Pudukudy, Z. Yaakob, and Z. S. Akmal, "Direct decomposition of methane over SBA-15 supported Ni, Co and Fe based bimetallic catalysts," *Appl. Surf. Sci.* **330**, 418–430 (2015).
- ²¹C. H. Yang, J. Li, Y. Lin, J. Liu, F. L. Chen, and M. L. Liu, "*In situ* fabrication of CoFe alloy nanoparticles structured $(\text{Pr}_{0.4}\text{Sr}_{0.6})_3(\text{Fe}_{0.85}\text{Nb}_{0.15})_2\text{O}_7$ ceramic anode for direct hydrocarbon solid oxide fuel cells," *Nano Energy* **11**, 704–710 (2015).
- ²²V. A. D. O'Shea, N. N. Menendez, J. D. Tornero, and J. L. G. Fierro, "Unusually high selectivity to C^{2+} alcohols on bimetallic CoFe catalysts during CO hydrogenation," *Catal. Lett.* **88**(3-4), 123–128 (2003).
- ²³X. Han, C. Yu, J. Yang, C. Zhao, H. Huang, Z. Liu, P. M. Ajayan, and J. Qiu, "Mass and charge transfer coenhanced oxygen evolution behaviors in CoFe-layered double hydroxide assembled on graphene," *Adv. Mater. Interfaces* **3**(7), 1500782 (2016).
- ²⁴M. Y. Zheng, X. W. Chen, R. H. Cheng, N. Li, J. Sun, X. D. Wang, and T. Zhang, "Catalytic decomposition of hydrazine on iron nitride catalysts," *Catal. Commun.* **7**(3), 187–191 (2006).
- ²⁵B. S. Li, L. L. Zhang, L. W. Chen, X. Y. Cai, L. F. Lai, Z. Wang, Z. X. Shen, and J. Y. Lin, "Graphene-supported non-precious metal electrocatalysts for oxygen reduction reactions: The active center and catalytic mechanism," *J. Mater. Chem. A* **4**(19), 7148–7154 (2016).
- ²⁶R. Razzaq, C. Li, M. Usman, K. Suzuki, and S. Zhang, "A highly active and stable $\text{Co}_4\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst for CO and CO_2 methanation to produce synthetic natural gas (SNG)," *Chem. Eng. J.* **262**, 1090–1098 (2015).
- ²⁷R. B. Anderson, "Iron nitrides as fischer-tropsch catalysts," *Adv. Catal.* **5**, 355–384 (1953).
- ²⁸Z. Yao, X. Zhang, F. Peng, H. Yu, H. Wang, and J. Yang, "Novel highly efficient alumina-supported cobalt nitride catalyst for preferential CO oxidation at high temperatures," *Int. J. Hydrogen Energy* **36**(3), 1955–1959 (2011).
- ²⁹E. C. Mattson, D. J. Michalak, W. Cabrera, J. F. Veyan, and Y. J. Chabal, "Initial nitride formation during plasma-nitridation of cobalt surfaces," *Appl. Phys. Lett.* **109**(9), 091602 (2016).
- ³⁰S. Sato, H. Honjo, S. Ikeda, H. Ohno, T. Endoh, and M. Niwa, "Evidence of a reduction reaction of oxidized iron/cobalt by boron atoms diffused toward naturally oxidized surface of CoFeB layer during annealing," *Appl. Phys. Lett.* **106**(14), 142407 (2015).
- ³¹K. I. Hadjiivanov, "Identification of neutral and charged N_xO_y surface species by IR spectroscopy," *Catal. Rev.* **42**(1-2), 71–144 (2000).
- ³²R. Newman and R. M. Chrenko, "Infrared absorption from L-S splittings in Co^{2+} salts," *Phys. Rev.* **115**(5), 1147–1152 (1959).
- ³³M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, and R. S. Smart, "Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co, and Ni," *Appl. Surf. Sci.* **257**(7), 2717–2730 (2011).
- ³⁴L. I. Johansson, H. I. P. Johansson, and K. L. Hakansson, "Surface-shifted N 1s and C 1s levels on the (100) surface of TiN and TiC," *Phys. Rev. B* **48**(19), 14520–14523 (1993).
- ³⁵L. I. Johansson and H. I. P. Johansson, "Core level study of NbC(100) and NbN(100)," *J. Electron Spectrosc. Relat. Phenom.* **80**, 237–240 (1996).
- ³⁶C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. H. Raymond, and L. H. Gale, "Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis," *Surf. Interface Anal.* **3**(5), 211–225 (1981).
- ³⁷F. Schrettle, C. Kant, P. Lunkenheimer, F. Mayr, J. Deisenhofer, and A. Loidl, "Wüstite: Electric, thermodynamic and optical properties of FeO ," *Eur. Phys. J. B* **85**(5), 164 (2012).
- ³⁸C. T. Seagle, W. Zhang, D. L. Heinz, and Z. Liu, "Far-infrared dielectric and vibrational properties of nonstoichiometric wüstite at high pressure," *Phys. Rev. B* **79**(1), 014104 (2009).
- ³⁹A. M. Jubb and H. C. Allen, "Vibrational spectroscopic characterization of hematite, maghemite, and magnetite thin films produced by vapor deposition," *ACS Appl. Mater. Interfaces* **2**(10), 2804–2812 (2010).
- ⁴⁰W. G. Wang, J. Jordan-sweet, G. X. Miao, C. Ni, A. K. Rumaiz, L. R. Shah, X. Fan, P. Parsons, R. Stearrett, E. R. Nowak, J. S. Moodera, and J. Q. Xiao, "*In-situ* characterization of rapid crystallization of amorphous CoFeB electrodes in CoFeB/MgO/CoFeB junctions during thermal annealing," *Appl. Phys. Lett.* **95**(24), 242501 (2009).