

Observation of boron diffusion in an annealed Ta/CoFeB/MgO magnetic tunnel junction with standing-wave hard x-ray photoemission

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The CoFeB/MgO system shows promise as a magnetic tunnel junction with perpendicular magnetization and low critical current densities for spin-torque driven magnetization switching. The distribution of B after annealing is believed to be critical to performance. We have studied the distribution of B in a Ta/Co_{0.2}Fe_{0.6}B_{0.2}/MgO sample annealed at 300 °C for 1 h with standing-wave hard x-ray photoemission spectroscopy (SW-HXPS). Comparing experimental rocking curve data to x-ray optical calculations indicates diffusion of 19.5% of the B uniformly into the MgO and of 23.5% into a thin TaB interface layer. SW-HXPS is effective for probing depth distributions in such spintronic structures. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4766351>]

The development of magnetic tunnel junctions (MTJs) for practical application involves the study of complex multi-layer structures in which buried interfaces and the distributions of the different atomic species in them play a critical role.¹⁻³ An optimal MTJ should have three essential characteristics: high thermal stability on the nanoscale, a high tunnel magnetoresistance (TMR) ratio, and a low current density across the ferromagnet-to-insulator interface when switching the magnetization via the spin-transfer-torque mechanism.²

A recent study by Ikeda *et al.* reveals that MTJs with the Ta/CoFeB/MgO/CoFeB/Ta structure satisfy these requirements.² Furthermore, it has been demonstrated that a low value for switching current can be achieved in CoFeB/MgO MTJs with perpendicular magnetic anisotropy (PMA) at the CoFeB/MgO interface.⁴ The B is initially present as CoFeB to maintain an amorphous layer with very smooth surface for subsequent optimal MgO (001) textured growth. Post-deposition annealing of such MTJs is necessary to drive the boron atoms out of the initially amorphous CoFeB layer, causing crystallization of the ferromagnetic layer into bcc CoFe(001) at the MgO interface. This crystallization is found to improve the TMR owing to enhanced coherent tunneling between CoFe(001) and MgO(001). The distribution of B in

Ta, CoFeB, and MgO after annealing at different temperatures and for different times is thus a critical parameter for fine-tuning the interface PMA, and has been the topic of several prior studies.⁵⁻⁸ It is thus important to characterize the buried layers and interfaces in this system with element specificity and sub-nm depth resolution.

To better understand the structure, chemistry, and magnetism in these buried layers, a nondestructive materials characterization technique is needed. One such method is standing-wave (SW) excited hard x-ray photoemission spectroscopy (HXPS, HAXPES), which has been already proven to be an effective materials characterization tool for other magnetic multilayer samples.⁹⁻¹² The standing wave is generated by Bragg reflection from a synthetic multilayer mirror on which the sample is deposited, and can be scanned vertically through the sample by varying the incidence angle around the Bragg angle: a rocking curve (RC) scan. Such scans of different core-level intensities thus provide much enhanced element-specific depth resolution compared, for example, to more classic angle-resolved x-ray photoelectron spectroscopy (ARXPS) measurements. Using hard x-rays for excitation also permits studying deeply buried layers and interfaces due to the larger inelastic mean free paths of 60–80 Å for the photoelectrons in this study. The present

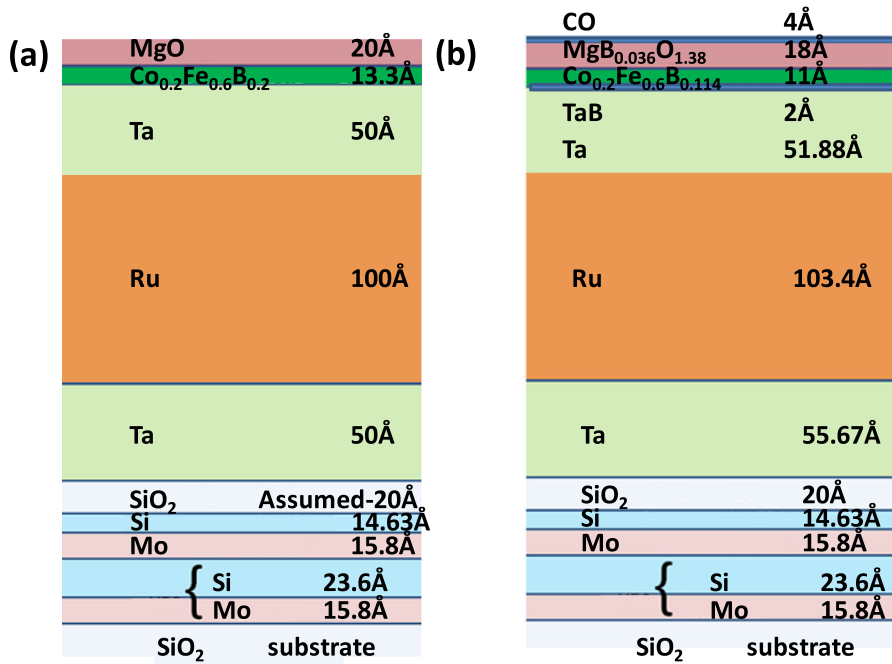


FIG. 1. (a) The nominal as-deposited geometry of the sample, with no allowance for the effects of annealing. (b) The final geometry of the annealed sample, resulting from optimized fits of x-ray optical theory to core-level rocking curves.

study involved comparing SW-HXPS experimental data with photoemission theory including all x-ray optical effects¹³ to explore the structure/properties relationship in the Ta/CoFeB/MgO/CoFeB/Ta system.

The multilayer mirror substrate was prepared at the LBNL Center for X-ray Optics and consisted of 60 bilayers of Si (23.6 Å)/Mo(15.8 Å); the top Si layer of this mirror had been air-exposed, which should lead to about 20 Å of native oxide. The period of the standing wave inside the sample will be very close to the bilayer thickness of $23.6 + 15.8 = 39.4$ Å, as verified by dynamical x-ray optical calculations. Onto the top surface of this mirror, as shown in Fig. 1(a), a five-layer sample of Ta/Ru/Ta/Co_{0.2}Fe_{0.6}B_{0.2}/MgO was deposited, which corresponds to the lower half of a MTJ. The nominal as-deposited geometry is shown in Fig. 1(a). The sample was then annealed at 300°C for 1 h, a treatment which in prior work has been shown to yield a high, near-

maximum, TMR ratio.^{8,14} Fig. 1(b) results from a fit to the data and will be discussed later.

Hard x-ray photoemission spectra were obtained from core levels of all elements in this sample at Beamline BL15XU of SPring-8.¹⁵ The p-polarized hard x-ray photon energy was set to 5953 eV, the angle between x-ray incidence and photoelectron exit was fixed at 90°, and x-ray incidence angles varied between 1.5° and 1.7° so as to scan over the Bragg condition. The energy resolution was found to be 230 meV, as determined by an Au Fermi-edge measurement.

As shown in typical core-level spectra in Fig. 2, both the B 1s and Ta 4f peaks show clear evidence of three chemically shifted components. For B 1s, two components are resolved: one at 187.8 eV that is associated with the CoFeB layer and with B that has reacted with Ta (“main” peak) and one at 191.8 eV associated with a more oxidized form of B in MgO (“oxide” peak); these assignments are consistent

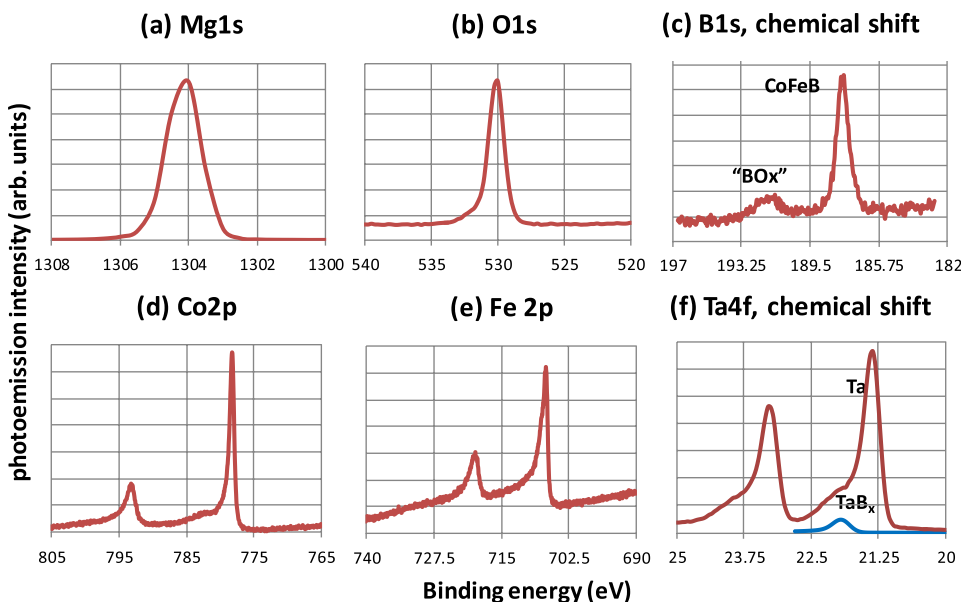


FIG. 2. Experimental x-ray photoelectron spectra for all of the elements in the Ta/CoFeB/MgO junction. Chemical shifts in B 1s and Ta 4f are observed.

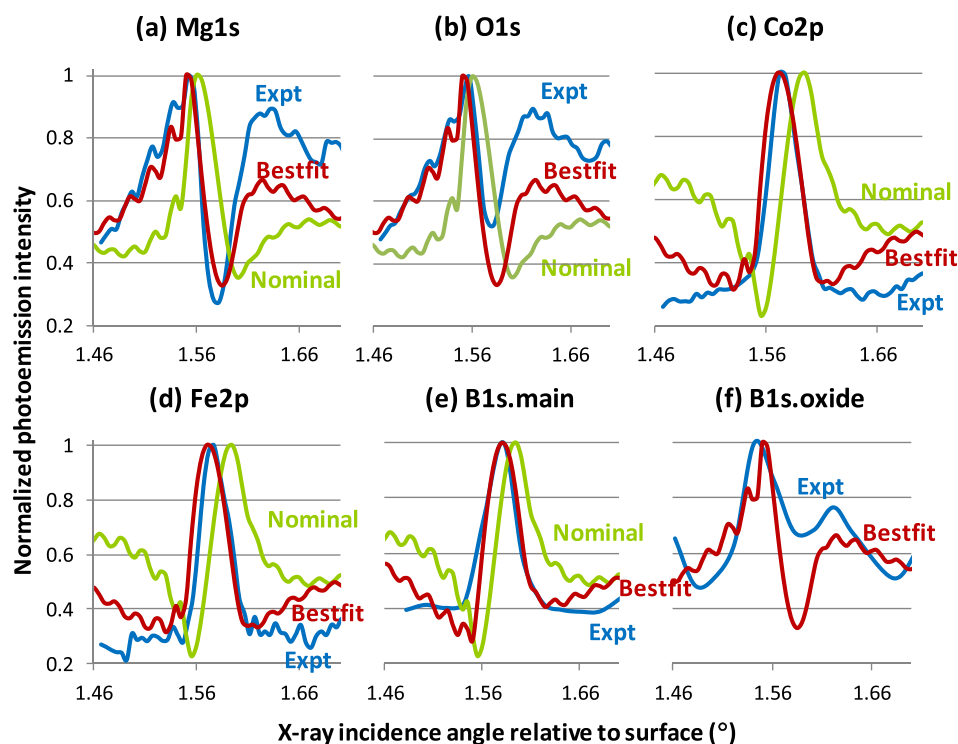


FIG. 3. Rocking curves: experiment vs. theory, from experiment and theory for the nominal starting sample configuration and the final best fit configuration.

with a recent soft x-ray photoemission study by Jang *et al.*¹⁴ The third component for B that has reacted with Ta can be resolved in the Ta 4f spectrum, consistent with a recent non-SW HXPS study by Kozina *et al.* at somewhat higher resolution.¹⁶ The Mg 1s spectrum has a high-binding energy shoulder that was found via RC analysis to be the “bulk” component, with a “surface” component about ~ 0.2 eV lower in binding energy near the top of this air-exposed layer.¹⁷ O 1s is narrow and featureless, although its RC also showed a similar chemical shift near the surface.¹⁷ The spectra for Co 2p and Fe 2p are narrow and similar to those of the metallic elements, showing no evidence of oxidation.¹⁸

The experimental rocking curves are shown in Fig. 3. In deriving intensities, a Shirley inelastic background¹⁹ was subtracted, and the spectra then fit with Voigt functions using the IgorPro software. The experimental data were then compared with theoretical calculations based on a specially written program allowing for all x-ray optical effects,¹³ and overall core-level intensities were also calculated with the XPS simulation program SESSA.²⁰ In fitting the calculated RCs to the experimental data, conservation of B and Si atoms were required to allow for the diffusion of B outward from the CoFeB and into MgO and Ta, as well as the prior oxidation of part of the top Si layer of the mirror, respectively.

Concentration gradients at interfaces were also required to be atom-conserving. A large number of possible variations in layer thicknesses and concentration gradients were simulated, including, e.g., B diffusing and reacting non-uniformly through the MgO layer, and comparing experiment and theory via chi-squared reliability factors. Finally, we arrive at the best-fit sample geometry shown in Fig. 1(b), and estimated errors of $\sim \pm 2$ Å in most of the thicknesses shown.

In Fig. 3, each experimental RC is compared to the calculated RC for the nominal geometry as synthesized, and to the RC for the best-fit geometry. All RCs in Fig. 3 have been normalized to unity at the maximum intensity of the given

Bragg peak so as to directly show the fractional max-min excursions, which are very large in the experimental data, being Mg 1s: $\sim 70\%$, O 1s: $\sim 50\%$, Co 2p: $\sim 70\%$, Fe 2p: $\sim 70\%$, B 1s main and oxide: 60% ; the calculated RCs also show similar degrees of modulation. Also apparent in the rocking curves for Mg 1s, O 1s, and somewhat weaker in Co 2p are Kiessig fringes that are caused by x-ray reflection from the top and bottom surfaces of the multilayer mirror.¹² There is less structure in the B RCs due to a significantly smaller number of angular data points taken for this much weaker spectrum (12 compared to 49 for the other RCs). Overall, there is excellent agreement between theory and experiment for our final best-fit configuration, including the prediction of Kiessig fringes for Mg 1s, O 1s, and Co 2p, whereas the match between experiment and nominal as-deposited theory is very poor, with several rocking-curve peaks out of phase.

The B 1s oxide RC, while not showing as deep a minimum as those of Mg 1s and O 1s, at least partially due to the lower number of data points, nonetheless strongly resembles them, suggesting rather uniform B diffusion throughout the MgO layer. This conclusion is supported by other x-ray optical calculations involving gradients of B in the MgO, as well as separate ARXPS measurements with 2.2 keV excitation (data not shown here).¹⁷

The near-identical lineshape of the RCs for Fe 2p and Co 2p implies the same depth distribution of these atoms within the CoFeB layer. The strong similarity between the B 1s main peak and those of Fe and Co further implies that those B atoms still within CoFeB are very uniformly distributed within this layer.

Finally, by analyzing the actual relative intensities of the various core peaks, including self-consistency checks between x-ray optical and SESSA simulations, we can say that about 19.5% uniformly into the MgO layer and about 23.5% has gone into a thin TaB-like layer on top of Ta, leaving for

these annealing conditions about 57% of the B still in the CoFeB layer, with an effective stoichiometry of $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.114}$.

Our experimental findings are thus consistent with recent results for a MTJ with a thicker CoFeB layer by Karthik *et al.*²¹ which imply that upon annealing the B atoms diffuse from the CoFeB layer into the MgO above and the Ta below, whereas the Co and Fe atoms do not leave the magnetic layer, nor change their relative positions in depth within the layer.¹⁶

We also find that the inclusion of a very thin layer of TaB atop the Ta layer improves the RC fit for the B 1s main peak (whose energy is not resolved from that of B in CoFeB), as well as for the Ta 4p peak (RC not shown here).¹⁷ The thickness of this TaB layer is also consistent with the relative intensity of the two chemically shifted peaks in Fig. 2(f).

Overall then, the as-deposited 13.3 Å of CoFeB annealed at 300 °C is found via our SW-HXPS determination to be 11 Å of $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.114}$. We also find 18 Å of $\text{MgB}_{0.036}\text{O}_{1.38}$ rather than the nominal starting value of 20 Å of MgO atop the CoFeB layer, with a “bulk” Mg/O stoichiometric ratio nearest the CoFeB of 1.00/1.38 being determined from Mg 1s/O 1s peak intensity ratios. This ratio analysis also allows for clear chemical shifts of Mg 1s and O 1s that are observed in their RC data (not shown here¹⁷), which result from a surface MgO layer that has clearly reacted with and adsorbed H₂O, CO, and other residual gas to pick up excess oxygen. Our stoichiometry for this layer thus disagrees somewhat with the results of a prior TEM/EELS study of a $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.22}/\text{MgO}$ sample with slightly longer annealing time,⁵ which proposed $\text{MgB}_{0.125}\text{O}_{1.5}$, agrees in finding the B atoms uniformly diffusing into MgO over a 1–2 nm distance, but disagrees in our finding more B atoms remaining in the CoFeB layer. However, our results are fully in agreement with a more recent STEM/EELS study of an annealed $\text{Co}_{0.19}\text{Fe}_{0.585}\text{B}_{0.22}/\text{MgO}$ MTJ by Kodzuka *et al.*,⁸ although the annealing conditions (1 h at 450 °C) were stronger than ours, and their images show somewhat less B remaining in the CoFeB layer, as might be expected from the higher temperature anneal. We thus conclude that significant B can remain in the CoFeB layer, and that outward diffusion from it occurs very nearly uniformly into a thin MgO layer of 1–2 nm thickness.

We have thus also demonstrated in this study that SW-HXPS is a non-destructive research tool which can be used together with other methods for the optimization of a variety of materials and nanostructures for spintronics and other applications.

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¹S. Ikeda, J. Hayakawa, Y. M. Lee, F. Matsukura, Y. Ohno, T. Hanyu, and H. Ohno, *IEEE Trans. Electron Devices* **54**, 991 (2007).

²S. Ikeda, K. Miura, H. Yamamoto, K. Mizunuma, H. D. Gan, M. Endo, S. Kanai, J. Hayakawa, F. Matsukura, and H. Ohno, *Nature Mater.* **9**, 721 (2010).

³C. Felser, G. H. Fecher, and B. Balke, *Angew. Chem., Int. Ed.* **46**, 668 (2007).

⁴M. Endo, S. Kanai, S. Ikeda, F. Matsukura, and H. Ohno, *Appl. Phys. Lett.* **96**, 212503 (2010).

⁵J. J. Cha, J. C. Read, W. F. Egelhoff, Jr., P. Y. Huang, H. W. Tseng, Y. Li, R. A. Buhrman, and D. A. Muller, *Appl. Phys. Lett.* **95**, 032506 (2009).

⁶S. S. Mukherjee, D. MacMahon, F. Bai, C.-L. Lee, and S. K. Kurinec, *Appl. Phys. Lett.* **94**, 082110 (2009).

⁷S. Ikeda, J. Hayakawa, Y. Ashizawa, Y. M. Lee, K. Miura, H. Hasegawa, M. Tsunoda, F. Matsukura, and H. Ohno, *Appl. Phys. Lett.* **93**, 082508 (2008).

⁸M. Kodzuka, T. Ohkubo, K. Hono, S. Ikeda, H. D. Gan, and H. Ohno, *J. Appl. Phys.* **111**, 043913 (2012).

⁹S.-H. Yang, B. S. Mun, N. Mannella, S.-K. Kim, J. B. Kortright, J. Underwood, F. Salmassi, E. Arenholz, A. Young, Z. Hussain, M. A. Van Hove, and C. S. Fadley, *J. Phys.: Condens. Matter* **14**, L407 (2002).

¹⁰S.-H. Yang, B. C. Sell, and C. S. Fadley, *J. Appl. Phys.* **103**, 07C519 (2008).

¹¹C. S. Fadley, *J. Electron Spectrosc. Relat. Phenom.* **178–179**, 2 (2010).

¹²A. X. Gray, C. Papp, B. Balke, S.-H. Yang, M. Huijben, E. Rotenberg, A. Bostwick, S. Ueda, Y. Yamashita, K. Kobayashi, E. M. Gullikson, J. B. Kortright, F. M. F. de Groot, G. Rijnders, D. H. A. Blank, R. Ramesh, and C. S. Fadley, *Phys. Rev. B* **82**, 205116 (2010).

¹³S.-H. Yang, “Making use of x-ray optical effects in photoelectron-, Auger electron-, and x-ray emission spectroscopies: total reflection, standing-wave excitation and resonant effects” (submitted); S.-H. Yang, A. X. Gray, A. M. Kaiser, B. S. Mun, B. C. Sell, J. B. Kortright, and C. S. Fadley, *J. Appl. Phys.* (submitted).

¹⁴Y. Jang, C. Nam, K.-S. Lee, B. K. Choa, Y. J. Cho, K.-S. Kim, and K. W. Kim, *Appl. Phys. Lett.* **91**, 102104 (2007).

¹⁵S. Ueda, Y. Katsuya, M. Tanaka, H. Yoshikawa, Y. Yamashita, S. Ishimaru, Y. Matsushita, and K. Kobayashi, *AIP Conf. Proc.* **1234**, 403 (2010).

¹⁶X. Kozina, S. Ouardi, B. Balke, G. Stryganyuk, G. H. Fecher, C. Felser, S. Ikeda, H. Ohno, and E. Ikenaga, *Appl. Phys. Lett.* **96**, 072105 (2010).

¹⁷A. Greer, “Hard X-ray Standing-Wave Photoelectron Spectroscopy Study of CoFeB/MgO Magnetic Tunnel Junction Multilayers,” Ph.D. thesis, University of California Davis (to be published).

¹⁸P. C. J. Graat and M. A. J. Somers, *Appl. Surf. Sci.* **100/101**, 36–40 (1996); K. Hirokawa, F. Honda, and M. Oku, *J. Electron Spectrosc. Relat. Phenom.* **6**, 333–345 (1975).

¹⁹D. A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).

²⁰W. Smekal, W. S. M. Werner, and C. J. Powell, *Surf. Interface Anal.* **37**, 1059 (2005).

²¹S. V. Karthik, Y. K. Takahashi, T. Ohkubo, K. Hono, S. Ikeda, and H. Ohno, *J. Appl. Phys.* **106**, 023920 (2009).