Role of Boron diffusion in CoFeB/MgO magnetic tunnel junctions

Sumanta Mukherjee,¹ Ronny Knut,² S. M. Mohseni,^{3,4} T. N. Anh Nguyen,^{3,5} S. Chung,⁶ Q. Tuan Le,³ Johan Åkerman,^{3,7} Johan Persson,³ Anindita Sahoo,^{1,8} Abhijit Hazarika,¹ Banabir Pal,¹ Sebastian Thiess,⁹ Mihaela Gorgoi,¹⁰ P. S. Anil Kumar,⁸ Wolfgang Drube,⁹ Olof Karis,² and D. D. Sarma^{1,2,11,*}

¹*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*

²*Department of Physics and Astronomy, Box 516, 75120 Uppsala, Sweden*

³*Materials Physics, School of ICT, KTH Royal Institute of Technology, Electrum 229, 164 40 Kista, Sweden*

⁴*Department of Physics, Shahid Beheshti University, Tehran, Iran*

⁵*Spintronics Research Group, Laboratory for Nanotechnology (LNT), VNU-HCM, Ho Chi Minh City, Vietnam*

⁶*Materials Physics, School of ICT, KTH Royal Institute of Technology, Electrum 229, 164 40 Kista, Sweden.*

⁷*Department of Physics, University of Gothenburg, Gothenburg, Sweden*

⁸*Department of Physics, Indian Institute of Science, Bangalore 560012, India*

⁹*Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany*

¹⁰*Helmholtz Zentrum Berlin für Materialien und Energie GmbH,*

Albert Einstein Straße. 15, 12489 Berlin, Germany

¹¹*Council of Scientific and Industrial Research - Network of Institutes for Solar Energy (CSIR-NISE), New Delhi 110001, India*

(Dated: December 30, 2014)

Several scientific issues concerning the latest generation read heads for magnetic storage devices, based on CoFeB/MgO/CoFeB magnetic tunnel junctions (MTJ's) are known to be controversial, including such fundamental questions as to the behavior and the role of B in optimizing physical properties of these devices. Quantitatively establishing the internal structures of several such devices with different annealing conditions using hard X-ray photoelectron spectroscopy, we resolve these controversies and establish that the B diffusion is controlled by the capping Ta layer, though Ta is physically separated from the layer with B by several nm. While explaining this unusual phenomenon, we also provide an insight into why the tunneling magnetoresistance (TMR) is optimized at an intermediate annealing temperature, relating it to B diffusion, coupled with our studies based on X-Ray diffraction (XRD) and magnetic studies.

I. INTRODUCTION

Magnetic tunnel junctions (MTJ) are of great importance due to their application in spin transfer torque based devices, e.g. magnetic random access memory (MRAM), high-frequency microwave sources, and in magnetic sensors [1–6]. Presently, sensors used in modern disk drives rely on tunnel magnetoresistance (TMR) in trilayer CoFeB/MgO/CoFeB structures, which succeeds earlier generation devices based on CoFe [4, 7]. While device fabrication has been empirically refined to meet strict quality demands, the fundamental understanding of the modifications in the TMR structure introduced by various optimization processes, e.g. post-annealing [8–16], resulting in a different magnitude of the TMR [10, 11], is still missing. In particular, the behavior of boron, apparently playing a crucial role for high magnetoresistance has remained controversial in spite of extensive investigations [12, 13, 15–24]. For example, it has been suggested that B diffusion is integral to the creation of a textured CoFe alloy and consequently high TMR. Many studies claim that boron diffuses into the

MgO tunnel barrier [12, 13, 15, 18, 19, 21–23, 25], where its presence is suggested to be detrimental [23, 24] to high TMR due to symmetry breaking of the barrier. Some reports, however, relate the improved TMR to diffusion of B into MgO [18, 22, 26]. For example, theoretical studies have suggested that the band structure of MgO-B also can provide a route for coherent tunneling of electrons and the diffusion of boron may even be beneficial for the TMR in the device [26]. Other reports [16, 20] claim that B rather migrates away from MgO, into the seed/cap layer resulting into TaB favoring high TMR [16, 17]. Thus, while great steps have been made improving device performances substantially, there are significant gaps in our understanding of these device structures. We have used hard x-ray photoelectron spectroscopy (HAXPES) [27–31] to investigate a series of TMR structures. HAXPES studies performed with photon energies even in excess of 10 keV, allows the probing depth to reach 50 nm or more. This allows the investigation of the electronic structure of buried interfaces [16, 21, 27–31] and enables an element-specific characterization of modifications of the interface structure with unsurpassed detail. By systematically studying the modifications of the chemical state of the constituents of the device for different structures and post-annealing conditions, we are able to provide a detailed geometric interpretation of how elements diffuse and modify the structure. The HAXPES measurements are complemented by XRD and magnetic measure-

* Also at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; Electronic address: sarma@sscu.iisc.ernet.in

ments to derive a complete understanding of all aspects controlling physical properties of these samples.

II. EXPERIMENTAL SECTION

We have used three sets of samples: (i) a complete trilayer structure with a protective Ta cap on-top Ta(5)/Ru(10)/Ta(5)/CoFeB(5)/MgO(2)/CoFeB(1)/Ta(5) (Sample T); (ii) a bilayer of the form Ta(5)/Ru(10)/Ta(5)/CoFeB(5)/MgO(2) (Sample B-1); and (iii) a bilayer with Ta capping on top of the MgO, namely Ta(5)/Ru(10)/Ta(5)/CoFeB(3)/MgO(1)/Ta(1.8) (Sample B-2). All numbers in parentheses refer to layer thicknesses in nm. The samples were grown by means of DC and RF magnetron sputtering. The base pressure in the sputter system was 1.0×10^{-8} Torr. The Ta and the MgO layers were RF sputtered at 2.5 mTorr, and 1.5 mTorr, respectively. The CoFeB electrodes were DC sputtered at 5mTorr. Optimum Ta smoothness as a function of pressure was established by means of low angle x-ray reflectivity. MTJ structures grown under same conditions have been independently characterized for their TMR as a function of post-annealing temperature. We find the maximum TMR value averaged over the whole wafer to be around 100% with highest TMR value of 235% for annealing around 300°C (See results and discussion section). HAXPES experiments were performed at the HIKE experimental station at KMC-1 bending magnet beam-line [29] in BESSY II, HZB, Berlin and at the HAXPES end-station at undulator beam-line P09 [30] of PETRA-III, DESY, Hamburg, Germany. Core level spectra (Co 2*p*, Fe 2*p*, B 1*s*, Mg 1*s*, O 1*s*, Ta 4*f*) were collected at different photon energies using a fixed, grazing incidence geometry (~ 7 degrees grazing incidence). Spectra were obtained for both the as-grown samples and after in-situ annealing for 20 minutes in subsequent steps at the following temperatures: $300 \pm 5^\circ\text{C}$, $420 \pm 10^\circ\text{C}$ and $520 \pm 10^\circ\text{C}$ at a base pressure of 10^{-9} Torr. Structural parameters were determined using an already established protocol based on photoelectron spectroscopy [32–35].

III. RESULTS AND DISCUSSION

Normalized HAXPES spectra collected for Fe 2*p*, and B 1*s* at different photon energies between 3000 eV to 5000 eV from Sample-T, representative of an actual TMR device structure, are shown in Figs. 1a and 1b, after subtracting a Shirley type background [36]. The spin orbit split 2*p* peaks of metallic Fe [12, 16, 21] can be seen (Fig. 1a) at binding energies (BE's) of 706.8 eV and 720.0 eV. The peak corresponding to metallic boron is found at a BE of 187.8 eV, along with a broad, low intensity feature at ~ 192.7 eV, due to various B-oxide species [12, 18, 20, 21]. This suggests a slight oxidation of the CoFeB layer during the growth of MgO, which was ac-

FIG. 1. (Color online) Normalized photoelectron spectra of (a) Fe 2*p* and (b) B 1*s* collected from the as-grown tri-layer MTJ sample-T at photon energies ranging from 3000 eV to 5000 eV. Panels 1c and 1d show comparisons of Fe 2*p* and B 1*s* spectra obtained at 4000 eV photon energy from the as-grown (black line) and 300°C annealed (red dots) samples. Photon energy dependencies of normalized photoelectron spectra of Fe 2*p* and B 1*s* collected from the 300°C annealed sample-T are shown in insets of panels 1c and 1d, respectively.

counted for in our analysis. A comparison of the Fe 2*p* and B 1*s* spectra, before and after annealing in-situ at the optimal $\sim 300^\circ\text{C}$, recorded using 4000 eV photon energy, is given in Figs. 1c and 1d. In contrast to many earlier reports [12, 18, 21], this comparison makes it clear that we do not observe any change in position or shape of the Fe 2*p* (Fig. 1c), B 1*s* (Fig. 1d) or in any of the other core level spectra (not shown). These observations are not specific to any particular excitation energy giving same conclusions when we compare the spectra obtained at other photon energies from this annealed sample (inset of Figs. 1c and 1d) with that of the unannealed sample. The spectral intensity ratios measured at different excitation energies for both the unannealed (circles) and the sample annealed at 300°C (diamonds) are shown in Fig. 2a. The intensity ratios between different core levels are almost identical for both the unannealed and the annealed samples. Our data thus clearly suggest that there is no significant diffusion of any of the elements comprising these TMR structures upon annealing at 300°C, which is the temperature we find optimizes TMR in our samples. The average TMR over the whole wafer and the resistance area product (RA) obtained from the as grown and annealed samples are given in Fig. 2b. We have followed the procedure described in Refs. [32–35] to obtain quantitative information on the layer stacking and thicknesses, using the spectral intensity ratios measured at different excitation energies.

Briefly, in this method the differential intensity contribution to a core level photoelectron spectrum of a particular atom contained in a volume element dV of the

sample at a depth z from the surface of the sample, can be expressed as

$$dI = n\sigma I_0 \exp(-z/\lambda \cos\theta) dV \quad (1)$$

where, λ is the mean free path of the photoelectron, σ is the photoionization cross section of that particular core level spectra, and the constant I_0 comes from the experimental condition, and depends on instrument geometry, photon flux, transmission function and angle of acceptance of the analyzer. θ is the photoelectron emission angle and n is the number density of that particular element within the volume element dV . The total photoemission spectral intensity of that particular core level then can be estimated by integrating Eqn. 1 over the whole volume of the sample. For the present thin film geometry the total photoemission intensity can be expressed as

$$I = \int_v dI = \sigma I_0 \int_0^z n(z) \exp(-z/\lambda \cos\theta) dz \quad (2)$$

In Eqn. 2, all symbols have the same definition as in Eqn. 1. For a thin film system containing an element A down to a depth of z_1 and element B from a depth of z_1 to z_2 , the intensity ratios at different photon energies can be expressed as

$$\begin{aligned} \frac{I_A(h\nu)}{I_B(h\nu)} &= \frac{\int_v dI_A(h\nu)}{\int_v dI_B(h\nu)} \\ &= \frac{\sigma_A(h\nu) \int_0^{z_1} n_A(z) \exp[-z/\{\lambda_A(h\nu)\cos\theta\}] dz}{\sigma_B(h\nu) \int_0^{z_2} n_B(z) \exp[-z/\{\lambda_B(h\nu)\cos\theta\}] dz} \end{aligned} \quad (3)$$

Where, $n(z)$, the number density of a particular element depends only on the depth, z , under the assumption of a laterally homogeneous, planner structure of the device and takes care of the specific model structure used. For example $n(z)$ will have the following form for a model structure with an atomically sharp interface between A and B, $n_A(z)$ and $n_B(z)$ will have the following forms

$$\begin{aligned} n_A(z) &= n_A & \text{for } 0 \leq z \leq z_1 \\ &= 0 & \text{for } z_1 \leq z \leq z_2 \\ n_B(z) &= 0 & \text{for } 0 \leq z \leq z_1 \\ &= n_B & \text{for } z_1 \leq z \leq z_2 \end{aligned}$$

Including the values of $n(z)$ in Eqn. 3 in this case, we obtain the equation for the intensity ratio as

$$\begin{aligned} \frac{I_A(h\nu)}{I_B(h\nu)} &= \frac{\int_v dI_A(h\nu)}{\int_v dI_B(h\nu)} \\ &= \frac{\sigma_A(h\nu) \int_0^{z_1} n_A \exp[-z/\{\lambda_A(h\nu)\cos\theta\}] dz}{\sigma_B(h\nu) \int_{z_1}^{z_2} n_B \exp[-z/\{\lambda_B(h\nu)\cos\theta\}] dz} \end{aligned} \quad (4)$$

Thicknesses z_1 and z_2 , defining the model used in this example, can be obtained by using Eqn. 4 to fit

FIG. 2. (Color online)(a) Intensity ratios between different core level photoelectron spectra obtained at different photon energies from the Trilayer sample-T, before (Circles) and after annealing (Diamonds) the sample at 300°C. (b) The average TdMR (averaged over the whole wafer) and the resistance area product (RA) obtained from the sample-T under different annealing conditions. (c) The thickness and nature of various layers in the capped trilayer sample-T, as deduced from the analysis of core level intensities as a function of the photon energy.

the experimentally obtained intensity at a number of different photon energies within a least-squared-error approach.

It can be easily seen that this quantitative estimation of the internal structure is not restricted only for sharp interfaces, since different kinds of structure can be modelled by proper choices of the parameter $n(z)$ to get the best fitting of the experimental intensity ratio. We have fitted the intensity ratios obtained from the photoelectron spectra of sample-T (Fig. 2b) and out of many modelled structures considered, the best fits to all the intensity ratios were obtained for the structures shown in Fig. 2c for Sample-T before and after annealing at 300°C. As evident from Fig. 2c, we observe basically no change between the structures of the as grown and 300°C annealed sample.

These results directly contradict a large number of results in the literature reporting diffusion of boron into MgO at 300°C [12, 13, 15, 18, 19, 21, 25]. However, there are a few reports in the literature [16, 17] that are in apparent agreement with our results. These contradictory results from samples that are apparently made the same way prompted us to scrutinize published data carefully. This revealed a systematic trend that experiments carried out on samples without a protective cap (for example Ta), show diffusion of boron into MgO [12, 13, 15, 21], whereas studies performed on

samples with a protective layer do not [16]. This generalization appears almost always to be in agreement with published results so far, though not identified by anyone; our present results on samples with Ta capping in Figs. 1 and 2c are also consistent with this trend. To test this hypothesis, we carried out further studies on a bilayer MTJ sample without Ta cap (Sample B-1) as well as on a Ta capped (Sample B-2) bilayer samples. The consequence of capping is clearly seen in the spectra of Fe $2p$ and B $1s$ shown in Figs. 3a - 3d for both the samples. The spectra collected from the as-deposited uncapped sample B-1 (Figs. 3a and 3b) are noticeably different from the capped trilayer sample, and the annealing strongly influences the core level spectra and hence the chemical structure of the layer stack. For example, the boron oxide content is higher in this sample and the oxidation of Fe is also evident in the Fe $2p$ spectrum. Upon annealing, the B $1s$ oxide species is found to increase markedly at the expense of the B $1s$ metallic peak intensity, whereas for Fe $2p$ the intensity of the metallic peak increases at the expense of the oxide intensity. The Co $2p$ spectrum (not shown) with an evidence of partial oxidation behaves similar to Fe $2p$. Additionally, the relative intensity of the B-oxide signal compared to the B-metal signal is invariably found to decrease with an increasing photon energy, while it was found to alter slightly with respect to Mg signal as illustrated for the annealed B-1 sample in the inset to Fig. 3a. These observations are readily attributed to the diffusion of boron into MgO as also suggested in the literature [12, 18, 21]. Our quantitative analysis of the intensity ratio reveals the internal structure of the uncapped bilayer sample B-1 before and after annealing as shown in Figs. 3e and 3f. The as deposited sample shows presence of a thin B-oxide layer (0.8 nm) at the interface between MgO (2.3 nm) and CoFeB (4.0 nm) layers (Fig. 3e). Upon annealing, B diffuses out from the CoFeB and forms a thick mixed layer of MgO and B-oxide, sandwiched between MgO and CoFeB layers. Such diffusion of B from the CoFeB matrix results in formation of a CoFe rich layer towards the bottom of the CoFeB layer (Fig. 3f). Corresponding results for the sample with the protective Ta cap (B-2) (Figs. 3c and 3d) show an almost complete suppression of the above-mentioned effects. The Fe $2p$ spectrum (Fig. 3c) of the as prepared sample is essentially free of any oxide signal and is unaffected by annealing, where the formation of boron oxide is largely suppressed (Fig. 3d) compared to the uncapped sample (Fig. 3b). The intensity ratios of various core levels obtained from the Ta capped bilayer sample were found to vary only slightly upon annealing, suggesting a very effective suppression of B migration upon capping, even for this bilayer sample. Thus, these results clearly establish a direct correlation between the B diffusion and oxidation in absence of a cap and a near-complete absence of such migration of B in presence of a cap of Ta layer irrespective of the sample being bi- or a tri-layer. These results rationalize all the contradictory

FIG. 3. (Color online) Panels 3a and 3b show Fe $2p$ and B $1s$ core level spectra collected from the uncapped bilayer sample-B1 at 3000 eV photon energy before (black) and after (red) annealing the sample at $300 \pm 5^\circ\text{C}$ for 20 minutes. Panels 3c and 3d show the same spectra for the Ta capped bilayer sample-B2 collected at 3600 eV. The inset of panel 3a shows the intensity ratio between B-oxide to B-metal (red triangles) and B-oxide to Mg (blue square) obtained from $300 \pm 5^\circ\text{C}$ annealed sample-B1 at different photon energies. The lines represent the intensity ratios for the best fitted structure, shown in 3f. The thickness and nature of various layers in the unannealed and annealed uncapped bilayer sample-B1 are shown in 3e and 3f. The numbers shown in the figures are in nanometer.

reports existing in the literature. The observation of the behavior of B being fundamentally altered by a layer of Ta, which is physically separated from the boron containing CFB layer by a several nm thick layer of MgO, may be understood as follows. The diffusion of B towards MgO, for example in the uncapped bilayer sample, is driven by the energy lowering associated with the oxidation of B. However, B cannot reduce stoichiometric MgO for energetic reasons. The only way B may be oxidized is by the presence of excess oxygen in the structure or by transportation towards the surface. It is important to note that we find evidence of extensive formation of carbonate species due to the reaction of the uncapped MgO with CO_2 . Such carbonates on top of MgO acts as a source of oxygen for B to oxidize, with B diffusing through MgO and an associated diffusion of oxygen ions towards the CFB layer, as described within the Mott-Cabrera theory of oxidation [37]. Thus, the

B diffusion and oxidation, as well as the conversion of the carbonate on the MgO surface to MgO must all go together, driven by the same chemical potential. We indeed find evidence of modifications of surface carbonate species with the oxidation and migration of B in the uncapped sample upon annealing. By capping the top surface with Ta, we cut off the oxygen source, essential for the oxidation and diffusion of B.

Few studies [16] report migration of B towards the opposite Ta layer instead of towards the MgO layer. These experiments are typically carried out on samples annealed at higher temperatures ($> 500^\circ\text{C}$). To gain further insights on the impact of high temperature annealing, we have carried out HAXPES experiments with step-wise annealing of the sample-T up to 520°C under UHV conditions. Figs. 4a and 4b show spectra of Fe 2*p* and B 1*s* core levels of Sample-T recorded at 4000 eV excitation energy and the effect of high temperature annealing. It is clearly seen (Fig. 4b) that the intensity of the B-oxide peak increases with respect to the metallic B 1*s* peak at higher annealing temperature, though the effect is much less pronounced compared to the uncapped B-1 sample. Changes are also found in the Fe 2*p* spectra, where the intensity at 709.9 eV *BE*, corresponding to the binding energy of Fe oxide [12, 18, 21], is depleted upon annealing. These observations suggest that the more electropositive B oxidizes itself by reducing the thin oxide layer of CoFe at the interface of CoFeB and MgO (See Fig. 2c). This makes a part of the B present in the CFB layers move towards the MgO layer. With additional measurements at a high photon energy of 8000 eV, to make the lower Ta/CFB interface visible, we also observed the formation of TaB, suggesting boron diffusion towards the lower interface at high annealing temperatures in agreement with other studies [16]. There are several possible consequences of our findings concerning boron diffusion. Diffusion of B into MgO can create pin holes in the MgO lattice [23], leading to leakage and decreased TMR. It can also alter the symmetry of the MgO lattice [24], again leading to a decreased TMR. It has furthermore been proposed that small amounts of Fe-oxide at the interface of CFB can improve the TMR significantly [22, 38]. The reduction of such interface oxide should therefore have a negative effect on the TMR. Considering the conditions for optimal TMR in our samples, with the results obtained from HAXPES, we arrive at the conclusion that the optimal annealing temperature for TMR is the maximum temperature where boron diffusion is still avoided. We have also looked into the effect of annealing on other physical properties of the TMR device, e.g. crystallinity and magnetic behavior, which plays an important roles in determining the TMR. For the as deposited sample the MgO(200) peak [10, 15] is very broad and weak (Fig. 4c), signifying the amorphous nature of the as-grown sample. Annealing to 300°C appears sufficient to crystallize the MgO layer. Higher temperature annealing does not change the FWHM of MgO(200) peak significantly. The

FIG. 4. Comparison of Fe 2*p* (a) and B 1*s* (b) spectra, collected for the tri-layer sample-T at 4000 eV photon energy before and after annealing the sample in-situ at 420°C for 20 minutes and subsequently to 520°C for 20 minutes. Panels 4c and 4d show the effect of annealing on the X-ray diffraction pattern and on the magnetization, respectively. The inset in panel 4d shows that the perpendicular anisotropy is removed upon annealing at high annealing temperature.

CFB peak, on the other hand, has very low intensity, making a detailed analysis based on the temperature dependence of the diffraction from CFB difficult. To obtain independent information on physical properties of the CFB layers, we therefore performed MOKE and magnetization measurements. Our magnetization data (Fig. 4d) suggest that, the sample annealed at 300°C already has strong in-plane magnetization and increases only slightly with an increasing annealing temperature. We conclude that annealing to higher temperatures does not lead to substantial improvements of the crystallinity of the MgO layer or of the magnetic properties of the CFB. Interestingly, there is a finite perpendicular magnetic anisotropy (PMA) present in all the samples, which completely vanishes at 520°C annealing, as shown by the polar MOKE data in the inset of Fig. 4d. Such a removal of perpendicular anisotropy could possibly lead to a decrease in the TMR value [14]. The depletion of Fe/Co oxide at the interface and the reduction of the PMA suggest a correlation between PMA and the existence of interfacial oxides. Theoretically it has been suggested that the PMA found in CFB/MgO/CFB structures are driven by hybridization to oxygen at the CFB/MgO interface [39]. Our observation principally supports this conclusion. However, our data suggest that the interfacial contribution to the PMA is due to the existence of a few Å thick partially oxidized CFB layer. This thin layer is reduced by boron when boron starts to diffuse into the MgO layer on annealing at a relatively high temperature. This suggests a very delicate balance of the stoichiometry of the interface to stabilize a PMA in CFB/MgO/CFB tunnel junctions.

IV. CONCLUSION

In conclusion, we have achieved quantitative descriptions of the internal structure of magnetic tunnel junctions annealed at various temperatures using hard x-ray photoelectron spectroscopy. Our data provides a resolution to apparently conflicting claims concerning B diffusion at moderate annealing temperatures. Our results establish that boron does not diffuse beyond one or two atomic planes at the interface of CoFeB and MgO under conditions typical for device fabrication, in a pristine well-capped trilayer sample. Higher temperature annealing allows a small fraction of boron to move into MgO,

reducing Fe and Co oxides present at the interface and forming B oxide. We have found indications that this reduction is detrimental to any perpendicular magnetic anisotropy in the system. Concerning the crystallization of MgO and magnetization of the CoFeB layer the results obtained from the samples studied by us conclude that 300°C annealing is sufficient.

V. ACKNOWLEDGMENTS

We thank the Department of Science and Technology, Government of India and Swedish Foundation for International Cooperation in Research and Higher Education (STINT) for financial support.

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