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Phys. Rev. Materials 3, 104410 — Published 14 October 2019
DOI: 10.1103/PhysRevMaterials.3.104410
Impact of the oxygen interdiffusion on spin-to-charge conversions at nonmagnetic metal/Bi oxide interfaces

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(Dated: 18 September 2019)

Spin-to-charge conversion at metal/oxide interface with the stacked structures of permalloy / (Cu or Ag) / Bi2O3 were systematically investigated by using the spin-pumping technique and cross-sectional transmission electron microscopy. Although the transport measurement reproduced the results in previous studies, the interfacial structure of (Cu or Ag)/Bi2O3 was found to change depending on the crystalline orientation of the Cu or Ag underlayer. While the Ag/Bi2O3 stacks with Ag (111) had steep interfaces, the formation of an nm-scale Cu-O layer can be found in the Cu/Bi2O3 interface, which should be the main origin of the sign inversion of the conversion coefficients between Cu/Bi2O3 and Ag/Bi2O3. This study stresses the importance of nanostructure identification to discuss spin-to-charge conversions at metal/oxide interfaces.

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I. INTRODUCTION

Exploration of the conversion mechanism between spin and charge currents is the essence of modern spintronics for realizing novel devices using spin-orbit torques (SOT). Early works attributed the giant spin Hall effect (SHE) to the large spin-orbit interaction (SOI) in bulk [1-5]. However, more recent investigations have indicated the importance of interfacial phenomena. In the past decade, the Rashba–Edelstein effect (REE) received much interest as a possible mechanism for interfacial spin-to-charge conversion [6-9]. Given the existence of large SOI, Fermi contours show a finite spin-split dispersion between the up and down spin states. When an interfacial charge current flows in a two-dimensional (2D) electron gas, helical spin polarization is accompanied by an in-plane spin accumulation perpendicular to the applied charge current. This non-equilibrium spin accumulation further induces a finite spin current at the interface, resulting in charge-to-spin conversion through the REE. The reverse process, i.e., spin-to-charge conversion at the Fermi contour, is called the inverse REE (IREE), in an analogy with the inverse SHE (ISHE).

Because REE originates from a virtual electric field applied at the Fermi contour [1], the field induced at the nonmagnetic metal (NM)/strong SOI insulator interface can feasibly substitute for a REE type charge-to-spin conversion source close to the interface. Based on this idea, Karube et al. [2] recently demonstrated anomalously efficient conversions at several Cu/Bi$_2$O$_3$ interfaces. Tsai et al. [3] also reported that an NM/Bi$_2$O$_3$ heterostructure could be used to control interfacial electron distribution by tuning the difference between the work functions across the interface. However, using oxide at the conversion interface usually carries a risk of unintended material oxidization. An et al. reported that the natural oxidization of Cu induced a finite spin torque in spite of the negligible SOI of Cu [4]. Such enhancements in the effective conversion factor have also been reported for other heterostructures, including Pt/CoFeB and Pt/Co [5], W/CoFeB [6], and Ta/Pt/Co [7]. It should be therefore difficult to distinguish the oxidization effect and the inherent IREE at metal/oxide interfaces, especially only by transport measurements.

In this study, we investigated spin-to-charge conversion efficiency at NM/Bi$_2$O$_3$ interfaces systematically to understand the conversion process. We discussed our results from four viewpoints to systemize the possible effects of NM/Bi$_2$O$_3$ interfaces:
(i) The effect of the crystalline orientation at the interface, by depositing a Ta buffer layer (BL) beneath the heterostructures,

(ii) The NM dependence, by comparing the effects of Cu and Ag spacers,

(iii) The effect of Bi segregation at the interface, by inserting a Bi layer between the NM and Bi oxide, and

(iv) The exact role of a capping Bi$_2$O$_3$ layer (CL), by replacing it with SiO$_2$.

The conversion efficiency at each interface was evaluated using the spin pumping technique, in the manner of IREE conversion. We also performed atomic level structure analyses at the interfaces by using high-resolution scanning transmission electron microscopy (STEM), with energy-dispersive X-ray spectroscopy (EDS).

We observed uniquely large conversion efficiencies at Cu/Bi$_2$O$_3$, Ag/Bi$_2$O$_3$ and Ag/Bi interfaces, as perfect reproductions of previous transport measurements [2,3,8]. Signs of the conversion constants were inverted between Ag and Cu spacers: the largest negative value was observed at the Cu/Bi$_2$O$_3$ interface while the largest positive one was obtained at the Ag/Bi interface where the largest spin splitting via IREE has been implied under (111) crystal orientation by using spectroscopic measurements [9,10]. The atomic level structure analyses have provided further insights of such nontrivial conversion mechanism at Bi$_2$O$_3$ including interfaces. Our Bi$_2$O$_3$ CLs formed amorphous Bi oxide (a-Bi-O) above the bottom polycrystalline FM and NM layers without Ta BLs. While once Ta BLs were inserted, the bottom layers were strongly aligned along the fcc (111) direction, which further promoted partial crystallization of $\alpha$-Bi$_2$O$_3$ at interfaces; however, the enhanced crystalline orientation resulted in a decreased conversion efficiency, indicating the limitations of the IREE model in transport measurements. Remarkably, significant O interdiffusion from Bi$_2$O$_3$ into Cu resulted in the formation of a Cu-O barrier at the interface. This study has revealed that the interfacial fine structure plays a more significant role in estimations of spin-to-charge conversion at NM/oxide interfaces than the choice of materials.
II. METHODS

All the multilayers were prepared on thermally oxidized silicon substrates in an ultrahigh vacuum chamber at a base pressure of $10^{-6}$ Pa at ambient temperature. We fabricated 16 different series of samples to respond to the tests required for filling all conditions from (i) to (iv). The base structure of our multilayer stacks was Fe$_{20}$Ni$_{80}$ (Py) (5 nm)/NM (Cu or Ag, 10 nm)/oxide capping layer (CL) (Bi$_2$O$_3$ or SiO$_2$). Film stacks with Ta (1 nm) underlayers were also prepared to examine the contribution of the (111) orientation to spin-charge conversion. We also examined the effect of inserting Bi (5 or 30 nm) between the NM and capping layers. All the metallic layers were deposited using radio frequency (RF) magnetron sputtering except for the Bi layer, which was deposited using an e-beam evaporator. The oxide capping layers were deposited by the e-beam evaporator from the stoichiometric sintered targets.

Figure 1 is a schematic illustration of the samples and measurement setup. Ferromagnetic resonance (FMR) in the Py layer was excited by using a waveguide placed 2 $\mu$m away from the sample to apply a perpendicular RF magnetic field, $h_{rf}$. The sample had wire widths ranging from 2 $\mu$m to 12 $\mu$m. The spin current caused by FMR was injected into the interface and converted into an electric dc voltage, $V$, through IREE. All measurements were performed at room temperature.

The vertical spin current density $J_s$, transferred from the Py layer to the NM/oxide interface, is scaled by the amplitude of $h_{rf}$ [11,12] as illustrated in Fig. 1(a):

$$J_s = \frac{2e}{h} \times \frac{h_G^{\uparrow \downarrow} h_{hf}^2}{8\pi^2 \alpha_{eff}^2} \left[ \frac{4\pi M_s \gamma + \sqrt{(4\pi M_s \gamma)^2 + 4\omega^2}}{(4\pi M_s \gamma)^2 + 4\omega^2} \right],$$  \hspace{1cm} (1)

where $\omega = 2\pi f$, $M_s$, $\gamma$, $e$, and $h$ are the angular frequency, saturation magnetization, gyromagnetic ratio, elementary charge, and reduced Planck constant, respectively. The amplitude of $J_s$ is characterized by the spin mixing conductance $G_{eff}^{\uparrow \downarrow}$ [13,14] arising from the difference between the damping in the studied sample ($\alpha_{eff}$) and the damping in a single reference layer ($\alpha_0$):

$$G_{eff}^{\uparrow \downarrow} = \frac{4\pi M_s e F}{\beta \mu_B} (\alpha_{eff} - \alpha_0),$$ \hspace{1cm} (2)
where \( t_F \), \( g \), and \( \mu_B \) are the thickness of the ferromagnetic layer, Landé factor, and Bohr magnetization, respectively. The converted charge current \( I_c \) is defined by a unit of 2D current density, \( j_c \):

\[
j_c = \frac{I_c}{w} = \frac{V}{wR},
\]

where \( w \), \( V \), and \( R \) are the width, the detected voltage, and the total resistance of the sample wire, respectively. The IREE induced spin-to-charge conversion constant \( \lambda_{\text{IREE}} \) is \( \lambda_{\text{IREE}} = j_c/\mathcal{J}_s \) in units of length. \( \lambda_{\text{IREE}} \) can also be expressed in terms of the Rashba parameter \( \alpha_R \) and the momentum relaxation time \( \tau \) at the interface [15]: \( \lambda_{\text{IREE}} = \alpha_R\tau/h \). However, an experimental estimation of \( \alpha_R \) using this expression is not a trivial exercise. It is because a determination of \( \tau \) for the metallic surface of Bi is difficult, unlike in the bulk [16]. In this study, we quantitatively evaluated IREE by using the conversion constant, \( \lambda_{\text{IREE}} \), instead of the Rashba parameter, \( \alpha_R \).

Thin foil specimens were prepared for STEM observations by using the lift-out technique with a focused ion beam (FEI Helios Nanolab 650). Microstructural characterization was performed using a transmission electron microscope (FEI Titan G2 80-200), with a high-resolution EDS element-mapping capability.

III. RESULTS AND DISCUSSION

First, the microfabricated device design was optimized. It should be noted that \( h_{\text{rf}} \) generated by a finite-scale waveguide is expected to have a non-uniform spatial distribution in the wired multilayers; \textit{i.e.}, the amplitude of \( h_{\text{rf}} \) becomes larger closer to the waveguide. Such an inhomogeneous \( h_{\text{rf}} \) triggers spatially nonuniform excitation of the FMR. Because \( \lambda_{\text{IREE}} \) scales with the gross area of the wire, as shown in Eq. (3), the spatial distribution of \( h_{\text{rf}}(\mathbf{r}) \) must be taken into account for the correct estimation of \( \lambda_{\text{IREE}} \). Figure 2(a) shows the resonance spectra of the rectified \( V \) for various wire widths \( w \), from 2 \( \mu \text{m} \) to 12 \( \mu \text{m} \), measured at the Py/Cu/Bi\(_2\)O\(_3\) microwire at 9 GHz. The monotonic decrease in the peak amplitude of \( V \) for wider samples indicates that \( h_{\text{rf}} \) may excite only one side of the wire edge, which would result in dissipative spin wave propagation along the \( y \)-direction.
The width dependence of the evaluated charge current density amplitude, $|j_c|$, has been plotted in Fig. 2(b). The experimental results follow an exponential decay curve, suggesting typical dissipative behavior along $w$. The attenuation length $\lambda$ was estimated as $\lambda = 6.79 \pm 0.22 \, \mu m$, which was comparable with that of the magnetostatic surface spin wave of Py [17]. The other outcome from these results is the large scalability of $|j_c|$ against $w$. The value of $|j_c|$ when $w = 2 \, \mu m$ is almost three times $|j_c|$ when $w = 12 \, \mu m$. Because $\lambda_{\text{IREE}} \propto |j_c|$, one also gets a 200% difference in conversion efficiency if the scale factor is not properly calibrated. Precise calibration requires knowledge of the spatial distribution of $h_{mf}(r)$, which appears in the injected current density $j_s$. Hereafter, all experimental results have been uniformly scaled with $w = 8 \, \mu m$, where values of $|j_c|$ at Cu/Bi$_2$O$_3$ interface were scaled comparable with those of Ref. 2.

To discuss the effect of crystalline orientation on IREE, the detailed consideration for Ta/Py/NM structures should be necessary. These structures are known to form strong (111) orientation for Py and NM layers without epitaxial growth [18,19]. However, Ta possesses a large spin Hall angle (SHA) [20,21] so the ISHE signal at the Ta/Py interface should be evaluated in advance. We prepared Ta (1 nm)/Py (5 nm)/Al (t) tri-layers, in which we continuously varied the Al layer thickness in the range of $0.0 \leq t \leq 5.0 \, \text{nm}$. The obtained resonance spectra for the ISHE voltage $V$ and induced $j_c$, with $t = 2 \, \text{nm}$ are presented in Fig. 3(a). The solid and open symbols are plots of $V$ under a positive field $H > 0$ and negative field $H < 0$, respectively. Finite resonance peaks were observed, but the sign-inverted ISHE component (the difference in voltage between the solid and open symbols) appeared very small, indicating that the Oersted-field-induced FMR excitation might be dominant. The ISHE components were quantified by fittings using a Lorentzian distribution and its derivative curves, and further converted into a charge current density, $j_c$, using Eq. (3). $j_c$ remained in the order of $\mu A/m$, and more than 100 times smaller than those of the Cu/Bi$_2$O$_3$ and Ag/Bi interfaces, as shown in Fig. 4(a). These results guarantee that the ISHE contribution at the Ta/Py interface is negligibly small in comparison to the signals from the NM/oxide interfaces. The origin of the small ISHE contribution can be explained by the large spin conductive mismatch between Py and the highly resistive, ultrathin Ta [22].

The dependences of the damping constant, $\alpha$, and $j_c$ on the Al thickness $t$ are shown in Fig. 3(b). The intrinsic damping constant, $\alpha$, of FMR, was evaluated from the
frequency dependence of the full width at half maximum (FWHM) as \( \Delta H = \Delta H_0 + (2\pi \alpha / \gamma) f \). They showed that the local minimum or maximum of \( \alpha \) and \( j_c \) at \( t = 2 \) nm coincided. For thinner Al regions (\( t < 2 \) nm), the Py top surface was no longer protected by Al, and oxidation of Py enhanced the FWHM of Py FMR, which results in an apparent increase in \( \alpha \). For thicker Al regions (\( t > 2 \) nm), a Ta/Py/Al/Al-O multilayer formed owing to natural oxidation of Al. This may induce an additional rectified voltage at the Al/Al\(_2\)O\(_3\) interface in the same manner as at the Cu/CuO interface [4]. Therefore, the value at \( t = 2 \) nm is expected to be the pure ISHE component at the Ta/Py interface. The referential damping constant \( \alpha_0 = 0.006 \pm 0.001 \) was also taken to deduce \( g_{\text{eff}}^{\uparrow\uparrow} \) at this point.

Figure 4(a) shows the resonance spectra of the rectified \( V \), and corresponding charge current density \( j_c \) for three different multilayers: Py/Cu/\( \text{Bi}_2\)O\(_3\), Py/Cu/SiO\(_2\), and Ta/Py/Ag/Bi/SiO\(_2\), respectively. The symmetric peak and dip show clear sign inversion for \( H > 0 \) and for \( H < 0 \); this means that ISHE- and/or IREE-induced conversion signals were dominant here. The amplitude of the resonance signal appeared especially large in the Py/Cu/\( \text{Bi}_2\)O\(_3\) and Ta/Py/Ag/Bi/SiO\(_2\) samples, which indicated efficient spin-to-charge conversions at the Cu/\( \text{Bi}_2\)O\(_3\) and Ag/Bi interfaces. Furthermore, the signs of \( j_c \) were different at these two interfaces, as reported previously [3]. The tiny signal obtained from the Py/Cu/SiO\(_2\) sample is consistent with a finite ISHE due to Cu oxidization [4,23,24], although neither the Py/Cu, nor the Cu/SiO\(_2\) interfaces themselves possessed little SOI as freestanding structures. These results are perfect reproductions of the nonconventional interface spin-charge conversions at Cu/Bi oxide interfaces reported in Ref. 2 and 3. The field dependence of the resonance frequency and the frequency dependence of FWHM \( \Delta H \) have been plotted in Fig. 4(b) and (c). The results shown in Fig. 4(b) indicate that the resonance spectra could be attributed to a uniform Kittel mode, \( f = 2\pi \sqrt{(H + H_c)(H + 4\pi M_c)} \), while those in Fig. 4(c) enabled us to evaluate the intrinsic damping constant, \( \alpha \), of the FMR for each sample.

Figure 5 summarizes \( \lambda_{\text{IREE}} \) for the 16 different samples measured at \( f = 9 \) GHz. The left panel shows the results for the samples with \( \text{Bi}_2\)O\(_3\) capping layers, while the right panel indicates the samples with SiO\(_2\) capping layers. The additional ISHE signal at the Ta/Py interfaces was calibrated from the results shown in Fig. 3. The insertion of the Ta BL improved (111) crystalline orientation of our Py/NM polycrystals, as
investigated by structure analysis below, whereas their conversion constants always decrease from those of non-inserted samples in any combinations of spacers and CLs. Note that our samples with or without Ta BL possessed polycrystalline or polycrystalline-amorphous interfaces, as indicated in the latter structure analysis, different from epitaxial interfaces used for angle-resolved photoemission spectroscopy (ARPES) measurements [25,26]. Our results clearly indicated IREE tends to decrease under (111) crystalline orientation in polycrystalline and polycrystalline-amorphous interfaces, and further stresses the importance of the nano-structure of realistic devices when discussing conversion efficiency.

The conversion phenomena exhibited the most dramatic changes at the interfaces including Bi$_2$O$_3$. Whereas the material dependences of almost all of the NM/SiO$_2$ interfaces remained flat, and their $|\lambda_{\text{IREE}}|$ were small (about 0.01), the NM/Bi$_2$O$_3$ interfaces had $\lambda_{\text{IREE}}$ values more than ten times larger (the black bars). Moreover, there were sign inversions between the Cu/Bi$_2$O$_3$ and Ag/Bi$_2$O$_3$, with and without the Ta BL [3]. These results clearly indicated that there was some kind of interfacial effect in the NM/Bi$_2$O$_3$ interfaces, and that it was not sensitive to the interfacial crystalline orientation. The origin of an unanticipated increase of the signal at Py/Cu/SiO$_2$ remained uncertain.

In the samples with a Bi insertion layer, the CL dependence was suppressed and $\lambda_{\text{IREE}}$ turned out to have positive values for all of the interfaces (the red bars in the figures). This implied that the interfacial conversion physics were governed by the NM/Bi interfaces, rather than by the top CLs. In other words, Bi segregations at interfaces cannot be the origin of unique variations with Bi$_2$O$_3$ CL. There are existing the strong debate of SHE of Bi [27,28,29], and relevant estimation of SHA for Bi only from above results should remained beyond the scope.

The solid symbols show previously reported $\lambda_{\text{IREE}}$, for which were measured using transport techniques, i.e., those of Cu/Bi$_2$O$_3$ by Karube et al. [2], Cu/Bi$_2$O$_3$ and Ag/Bi$_2$O$_3$ by Tsai et al. [3], Ag (111)/Bi by Sánchez et al. [8], Ag/Bi by Zhang et al. [10], and Cu/Bi by Isasa et al. [16]. Our results were comparable with these, showing particularly good agreement with those for Cu/Bi$_2$O$_3$ [2] and Ag (111)/Bi [8].

Because REE is essential for the spin splitting of the Fermi contours, it was necessary to perform a precise structural analysis that directly correlated with the
formation of the electrostatic potentials. Figure 6 shows the cross-sectional high-angle annular dark-field (HAADF)-STEM images, and integrated nanobeam electron diffraction (NBD) patterns of the Bi$_2$O$_3$, NM (Cu or Ag), and Py layers in (a) Py/Cu/Bi$_2$O$_3$, (b) Py/Ag/Bi$_2$O$_3$, and (c) Ta/Py/Ag/Bi$_2$O$_3$. The cross-sectional images illustrate continuous and non-epitaxial growth of NM/oxide interfaces in all multilayers, and the NBD patterns provide details relating to film crystallinity.

The NBD patterns of the Bi$_2$O$_3$ layers all contain typical halo rings caused by the amorphous structure, indicating formations of as-deposited a-Bi-O layers. While NM and Py have spotted patterns unique to their crystalline structure. The spotty patterns of NM and Py in Py/Cu/Bi$_2$O$_3$ (Fig. 6(a)) appear random, indicating that these layers have a non-oriented, polycrystalline nature. The diffraction pattern in the Ag layer of Py/Ag/Bi$_2$O$_3$ (Fig. 6(b)) and Ta/Py/Ag/Bi$_2$O$_3$ (Fig. 6(c)) is completely different: the (111) NBD spots appear much clearer, and NBD patterns of Ag and Py are identifiable along the [211], [110], and [110] fcc zone directions. This crystalline orientation is further enhanced with Ta BL, which results in clear peaks in the XRD profiles (not shown). The crystallography remains polycrystalline, but its crystalline growth direction is strongly aligned to (111). Also, the halo ring of a-Bi-O layer is switched to spotty patterns with Ta BL, corresponding to partial crystallization of Bi$_2$O$_3$ crystals there. Figure 6(d) shows the magnified STEM image of the Ag/Bi$_2$O$_3$ interface of Ta/Py/Ag/Bi$_2$O$_3$. Clear atomic columns are observed at the vicinity of the interface with Ag as shown by the arrows. NBD patterns obtained at these points (inset if Fig. 6(d)) are identifiable by monoclinic $\alpha$-Bi$_2$O$_3$, the stable crystal of Bi$_2$O$_3$ at ambient conditions [30,31]. These results indicate that interface formations of Bi$_2$O$_3$-deposited NM are quite sensitive to crystalline orientations of bottom NMs, modified by insertions of Ta BLs, and further imply the origin of unique variations in $\lambda_{\text{REE}}$ underneath Bi$_2$O$_3$ CL in Fig. 5 can be ascribed to the difference in interfacial states, from non-oriented polycrystalline Cu/a-Bi-O to Ag(111)/$\alpha$-Bi$_2$O$_3$.

Because Cu/Bi$_2$O$_3$ stacks are identified as polycrystalline-amorphous interfaces, the discussion provided in Ref. 3 on a freestanding $\alpha$-Bi$_2$O$_3$ crystal turns out to be irrelevant to our situation. To get more concrete insights into NM/oxide interfaces, high-resolution STEM images, EDS elemental maps, and line profiles of each element of (a) Py/Cu/Bi$_2$O$_3$, (b) Py/Ag/SiO$_2$, (c) Py/Ag/Bi$_2$O$_3$, and (d) Ta/Py/Ag/Bi$_2$O$_3$ were prepared
and have been presented in Fig. 7. It can be seen that almost all of the layers are well separated, and that steep interfaces form between Ta/Py, Py/NM, and NM/CL, independent of the NM and CL combination, although only the O layer of the Py/Cu/Bi$_2$O$_3$ sample diffused into the Cu layer (Fig. 7(a)). Such nanoscale interdiffusion resulted in the formation of an insulating Cu-O barrier between the Cu/a-Bi-O interfaces, which appears as the dark contrast enclosed by the red dotted line in Fig. 7(a).

We next focus on-line profiles of the elemental maps added on the right hands of the EDS maps. Here, the horizontal solid lines highlight the edge centers of each element (Bi, Si, O, Cu, and Ag) according to their fitted Boltzmann function. Nanometer-scale interdiffusion between O, Bi, and Cu was observed only at the Cu/Bi$_2$O$_3$ interface. The amplitude of the O interdiffusion was evaluated as a function of the distance between the O and Bi (Si) edge centers. Although the Cu/SiO$_2$ and Ag/Bi$_2$O$_3$ showed steep interfaces without any O interdiffusion, significant interdiffusion into the Cu layer was found in case of Cu/Bi$_2$O$_3$. The depth reached 1.6 ± 0.1 nm which should not be treated as the fine 2D interface. These results indicated that the peculiar spin structure of the Bi$_2$O$_3$ alloy assumed in Ref. 3, discussed as the origin of large conversion efficiency, could be no longer maintained at the interfaces in the present samples. Or rather, our results are in agreement with recent observations of the interfacial Rashba SOT, in terms of oxygen incorporation.

As summarized all insights from foregoing structure analysis with transport measurement, robust conditions of large anomalies in conversion at NM/Bi$_2$O$_3$ interfaces are determined. First, large but inverted conversions at Cu/Bi$_2$O$_3$ are attributed to strong interdiffusion of oxygen from Bi$_2$O$_3$. Second, large conversions at Ag/Bi$_2$O$_3$ are attributed neither IREE at Ag(111)/Bi interface, nor spin structure of α-Bi$_2$O$_3$ crystal. A notable point is, the freestanding Bi$_2$O$_3$ alloy is not fundamental at any anomalies there. Further questions arise from the results of (i) and (ii), regarding the origin of the sign inversion at the O inter-diffused Cu/Cu-O/a-Bi-O interface, and the enhanced $\lambda_{\text{IREE}}$ at non-oriented Ag / Bi interfaces.

Very recently, Gao et al. [24] reported that the field-like SOT changed significantly, and even switched sign, when the interfacial oxidation level at Py/CuO$_x$ bilayers was tuned. These results cannot directly compare with our ISHE and IREE signals obtained spin pumping method, but underlying FM dynamics, which will affect
spin current injection process also in our method, can be remarkably affected by Cu oxidization. We also refer to the orbital Hall effect (OHE) [32,33,34] predicted at several transition metals. Although no experimental observation of OHE at any metallic heterostructure was reported yet, such SOI free angular momentum transfer may affect an increase in spin to charge conversions. Further systematic studies will be required to clarify the origin of the large charge current there.

The reasons for the \( \lambda_{\text{IREE}} \) at non-oriented Ag/Bi interfaces being larger than at Ag (111)/Bi interfaces in Fig. 5 are also nontrivial. In terms of fine structure analysis, most previous reports on Ag/Bi interfaces using transport techniques [8,10] (including ours), could not claim to have achieved a perfect (111) crystalline orientation, because none had the required level of epitaxial flatness in ARPES [9]. Our study shows that the characteristics of Ag/Bi interfaces obtained in device structures should not be equivalently compared with those obtained ARPES measurements which reflect atomic level accuracy. That is, epitaxially grown Ag (111) might be required to make a precise comparison with the values of \( \lambda_{\text{IREE}} \) derived from transport measurements.

IV. CONCLUSION

In summary, the strong interfacial spin-to-charge conversion at NM (Cu or Ag)/Bi\(_2\)O\(_3\) interfaces was comprehensively examined by spin pumping measurements and atomic level structural analysis using HAADF-STEM imaging and EDS elemental mapping. We used four different criteria to distinguish bulky ISHE and interfacial IREE and revealed nontrivial effects from crystalline orientation and interfacial diffusion. Crystalline orientation significantly affects the interfacial formation when Bi\(_2\)O\(_3\) is deposited on the NM layer. \( \alpha \)-Bi\(_2\)O\(_3\) is crystallized only when bottom Ag layer is strongly aligned to the (111) direction while non-oriented Cu layer results in amorphous Bi oxide at its interface. Also, no inherent increase but small decrease in the IREE conversion efficiency is observed at crystallized Ag(111)/\( \alpha \)-Bi\(_2\)O\(_3\) interface, compared with NM/a-Bi-O interfaces. These results imply the existence in the extrinsic effects aside from interfacial contributions. Meanwhile, interfacial diffusion plays a crucial role in the sign inversions observed at the Cu/Bi\(_2\)O\(_3\) stack, forming Cu/Cu-O/a-Bi-O interface, which could be ascribed to enhanced intrinsic SOT at the Cu-O insulating interlayer. These
findings point to difficulties in comparing the results of transport measurements with those of surface ARPES measurements without an atomic level understanding of interfacial structure. Our work proposes a better understanding and engineering of efficient spin-to-charge interfacial conversion systems for future spintronic applications, through consideration of the inter-diffusion between NM/Bi oxide interfaces.

ACKNOWLEDGEMENTS

This work was partially supported by the Japan Society for the Promotion of Science, KAKENHI grant no. 17K18892, and JST, PRESTO grant no. JPMJPR18L3, Japan.
Fig. 1. (a) Schematic of spin-to-charge current conversion ascribed to IREE. Spin currents are generated by spin pumping of the Py layer under FMR, which travel through the NM layer and reach the interface. Spin-to-charge current conversion occurs owing to spin-momentum locking at the interface between the NM layer and CL. (b) Schematics of the measurement setup.
Fig. 2. (a) Resonance spectra of the rectified voltage $V$ for different wire widths $w$ of Py/Cu/Bi$_2$O$_3$ microwires. The excitation frequency $f = 9$ GHz. (b) $w$ dependence of the charge current density $|j_c|$. The solid curve is a fitting using an exponential decay curve.
Fig. 3. (a) Resonance spectra of the rectified voltage $V$ and the charge current density $j_c$, in Ta/Py/Al (2 nm). (b) Al thickness dependence of the Gilbert damping parameter $\alpha$ and charge current density $j_c$. The excitation frequency $f = 9$ GHz.
Fig. 4. (a) Resonance spectra for the rectified voltage $V$ and charge current density $j_c$ for $H > 0$ in various interfaces: (i) Py/Cu/Bl$_2$O$_3$, (ii) Py/Cu/SiO$_2$, and (iii) Ta/Py/Ag/Bi/SiO$_2$. Results for $H > 0$ are plotted as closed symbols, while those for $H < 0$ are plotted as open symbols. (b) Field dependences of resonance frequencies in each interface. Solid curves indicate a fitting using the Kittel formula. (c) Frequency dependences of FWHM $\Delta H$ for the spectrum at each interface. Solid lines are linear fittings.
Fig. 5. Conversion efficiencies $\lambda_{\text{REE}}$ in various interfaces. Black bars indicate the results for the basic structures (Ta)/Py/NM (Cu or Ag)/CL (Bi$_2$O$_3$ or SiO$_2$), while red bars show the results of structures with Bi inserted between NM and CL. The solid colored circles indicate results from previous experiments which used the same spin pumping techniques: Cu/Bi$_2$O$_3$ by Karube et al. [2], Cu/Bi$_2$O$_3$ and Ag/Bi$_2$O$_3$ by Tsai et al. [3], Ag (111)/Bi by Sánchez et al. [8], Ag/Bi by Zhang et al. [10], and Cu/Bi by Isasa et al. [16].
Fig. 6. Cross-sectional HAADF-STEM images and integrated NBD patterns for the Bi2O3, NM (Cu or Ag), and Py layers, in (a) Py/Cu/Bi2O3, (b) Py/Ag/Bi2O3, and (c) Ta/Py/Ag/Bi2O3. The NBD signals are integrated from 2 x 40 nm for Py, 5 x 40 nm for NM, and 10 x 40 nm for Bi2O3. (d) Magnified STEM image at Ag/Bi2O3 interface of (c) Ta/Py/Ag/Bi2O3. Inserted NBD signals are obtained at crystallized Bi2O3, as indicated by white arrows.
Fig. 7. High-resolution cross-sectional HAADF-STEM images at NM/oxide interfaces, and corresponding EDS maps for (a) Py/Cu/Bi$_2$O$_3$, (b) Py/Ag/SiO$_2$, (c) Py/Ag/Bi$_2$O$_3$, and (d) Ta/Py/Ag/Bi$_2$O$_3$. Line profiles of the elemental maps are plotted. Horizontal lines of the profiles exhibit edge centers for each element, obtained by Boltzmann function fittings.


