First-principles investigation of magnetocrystalline anisotropy oscillations in Co$_2$FeAl/Ta heterostructures

Junfeng Qiao,$^{1,2}$ Shouzhong Peng,$^{1,2}$ Youguang Zhang,$^{1,2}$ Hongxin Yang,$^3$ and Weisheng Zhao$^{1,2}$

$^1$Fert Beijing Institute, BDDBC, Beihang University, Beijing 100191, China
$^2$School of Electronic and Information Engineering, Beihang University, Beijing 100191, China
$^3$Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

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We report first-principles investigations of magnetocrystalline anisotropy energy (MCAE) oscillations as a function of capping layer thickness in Heusler alloy Co$_2$FeAl/Ta heterostructures. Substantial oscillation is observed in FeAl-interface structure. According to $k$-space and band-decomposed charge density analyses, this oscillation is mainly attributed to the Fermi-energy-vicinal quantum well states (QWS) which are confined between Co$_2$FeAl/Ta interface and Ta/vacuum surface. The smaller oscillation magnitude in the Co-interface structure can be explained by the smooth potential transition at the interface. These findings clarify that MCAE in Co$_2$FeAl/Ta is not a local property of the interface and that the quantum well effect plays a dominant role in MCAE oscillations of the heterostructures. This work presents the possibility of tuning MCAE by QWS in capping layers, and paves the way for artificially controlling magnetic anisotropy energy in magnetic tunnel junctions.

I. INTRODUCTION

With the increasing demand for high-speed and low-power-consumption storage devices, intensive researches have been made on spin-transfer-torque magnetic random access memory (STT-MRAM). The core structure of MRAM is magnetic tunnel junction (MTJ) which is composed of an insulating barrier sandwiched by two ferromagnetic (FM) electrodes. The relative orientation of two FM electrodes represents two states and can be utilized to store one bit information. To realize high storage density, the manufacturing process is scaling down to nanometer regime. However, the increasing process variations in the fabrication pose serious challenges to fundamental physics, especially magnetocrystalline anisotropy energy (MCAE), which is critical for the thermal stability of the relative magnetization orientation of two FM electrodes. Previous work reported that to achieve a retention time of 10 years, an interfacial perpendicular magnetic anisotropy (PMA) of 4.7 mJ/m$^2$ is required for device sizes scaling down to 10 nm. However, at present the most widely used FM electrode, CoFeB, can commonly reach an interfacial PMA of 1.3 mJ/m$^2$ when interfaced with MgO tunneling barrier. At the same time tunneling magnetoresistance (TMR) can reach a value of 120% in CoFeB/MgO/CoFeB MTJ which needs to be improved as well.

To further promote the development of STT-MRAM, other FM materials are under investigation. Heusler alloys are a big family of ternary intermetallic compounds with nearly 1500 members. According to their chemical composition, Heusler alloys can be separated into two classes, full Heusler with chemical composition X$_2$YZ ($L_2$$_1$ structure) and half Heusler XYZ ($C1_b$ structure), in which X and Y are transition metals, and Z is main group element. By virtue of the broad choices of elements and stoichiometry, many Heusler compounds exhibit interesting properties, such as half-metallicity, various Hall effect, thermoelectric effect, topological effect and superconductivity etc. Among Heusler alloys, Co$_2$FeAl (CFA) has attracted lots of attention due to its high spin polarization and low magnetic damping constant, which can reach up to 700% at 10 K and 330% at room temperature (RT) in Co$_2$FeAl/MgO/CoFe MTJ. Magnetic damping constant, $\alpha$, can reach as low as 0.001 which is beneficial for reducing STT switching current. Another merit of CFA is its fine lattice matching with MgO. As a result, epitaxial growth of CFA(001)$\parallel$MgO(001) has been achieved in experiment. All these advantages make CFA a promising candidate for MTJ electrode material. Regarding magnetic anisotropy energy (MAE) of CFA, experimental and theoretical results confirmed that the Co$_2$FeAl/MgO interface can reach around 1 mJ/m$^2$. However, as discussed above, MAE needs to be optimized further. Besides, it is crucial to find out effective ways to artificially control MAE.

Recently, experimental and theoretical results showed that heavy metals (HM) can induce large variations of physical properties including MAE when interfaced with FM materials. In practical MTJs, a buffer layer at the bottom and a capping layer on the top are necessary to improve and protect the FM/MgO/FM core structure. Consequently, the choice of capping layer provides us a unique way to control MAE of the whole structure. On the other hand, when the thickness of these multilayers reaches down to atomic scale, quantum mechanical (QM) effects start to dominate. One of the most well-known QM effect is quantum well (QW), in which the wave functions of the quantum particle are confined by potential

*weisheng.zhao@buaa.edu.cn
barriers and the energy levels are quantized. In spintronics, the milestone effect, giant magnetoresistance (GMR), and its closely related phenomenon, interlayer exchange coupling (IEC), are deeply related to QW. These effects have been successfully explained by quantum interferences due to reflections at the spacer boundaries. In terms of the influence of quantum well states (QWS) on MAE, early theoretical works, using tight-binding formalism and a perturbation treatment to spin orbit coupling (SOC), reported the oscillation of MAE with respect to Pd layer thickness in Co/Pd system. While there also exists other work which supports interfacial MAE in Pd/Co/Pd(111) structure. Other than HM Pd, MAE oscillations with respect to both Co and Cu were found in Co/Cu system. Since the IEC effects are prominent in these structures, the formation of QWS are well confirmed. Indeed, 10 years later, MAE oscillations were observed in Cu(001)/Co, Ag(001)/Pd, and Fe/Cu, Co/Cu structures, and the origin of these oscillations were attributed to QWS. Also, QWS induced oscillatory IEC was found in Co/MgO/Co PMA MTJ. Recent first-principles studies have correlated QWS with MCAE in Ag/Fe and IEC in Fe/Ag/Fe structures. These works indicate that the influence of QWS on magnetic properties, specifically MAE, may become salient in some structures.

In this paper, we report ab-initio calculations of MCAE in CFA/Ta structures and observe MAE oscillations associated with the Ta layer thickness. These oscillations are further proved as induced by both majority-spin and minority-spin QWS confined in Ta layers. The origin of the significant MCAE oscillation is attributed to the repeated traversing of QWS across Fermi energy and the large SOC of Ta. In all, QWS formed in the capping layer provide us a unique method to tune MAE in the MTJ structure.

II. METHODS

Calculations were performed using Vienna ab initio simulation package (VASP) based on projector-augmented wave (PAW) method and a plane wave basis set. The exchange and correlation terms were described using generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) parameterization. We used a kinetic energy cutoff of 520 eV and a Gamma centered Monkhorst-Pack k-point mesh of 25 × 25 × 1. The convergence of MCAE relative to k-point has been checked carefully, the variation of MCAE is about 0.05 meV when changing k-point mesh from 20 × 20 × 1 to 25 × 25 × 1, which is at least a magnitude smaller than the oscillation amplitude of MCAE. The energy convergence criteria of all the calculations were set as 1.0 × 10^{-7} eV, and all the structures were relaxed until the force acting on each atom was less than 0.01 eV/Å. All the structures have at least 15 Å vacuum space to eliminate interactions between periodic images. Bulk CFA has a cubic $L2_1$ crystal structure. After fully relaxing bulk structure in volume and shape, the lattice constant is found to be $a_{\text{bulk}} = 5.70$ Å, perfectly matches the experimental value 5.73 Å. For CFA/Ta heterostructure, an in-plane lattice constant of $a = a_{\text{bulk}}/\sqrt{2} = 4.03$ Å is adopted for the unit cell, which is rotated by 45 degrees from the conventional cell of bulk CFA. For all the CFA/Ta structures, 9 monolayers (ML) of CFA are used, and 1 to 12 ML of Ta layers are put on top of CFA, as shown in Fig. 1. We use CFA/Ta[$n$] to label structures of different Ta ML, where $n$ is the number of Ta ML, ranging from 1 to 12. As for the interface between CFA and Ta, there exist two kinds of configurations and both of them have been investigated. FeAl-CFA/Ta is used as the label when FeAl layer of CFA directly contact with Ta, while Co-CFA/Ta is used when Co layer of CFA contact with Ta.

![FIG. 1. Crystal structure of (a)FeAl-CFA/Ta[9], (b)Co-CFA/Ta[9], (c)FeAl-CFA/Ta[5] and (d)Co-CFA/Ta[5]. Only 4 structures are shown as illustrations. In other structures, only the numbers of Ta ML are varied, ranging from 1 to 12. The dashed green rectangle box highlights the area of the interfaces.](image-url)

To calculate MCAE, two-step procedures were adopted. Firstly, charge density was acquired self-consistently without taking into account SOC. Secondly, reading the self-consistent charge density, two non-self-consistent calculations were performed including SOC, with magnetization pointing towards the [100] direction and the [001] direction, respectively. Finally, MCAE was calculated by $MCAE = E^{[100]} - E^{[001]}$, positive MCAE stands for PMA while negative MCAE for in-plane magnetic anisotropy. To get a deeper understanding of the origin of oscil-
lotion, MCAE is decomposed into $k$-space. According to force theorem, the main contribution of MCAE originates from the difference of eigenvalues between two magnetization directions. Indeed, we found that the ion Ewald summation energy, Hartree energy, exchange correlation energy and external potential energy are exactly the same between two magnetization directions, the difference of total energy only comes from the difference of eigenvalue summation, this testifies the feasibility of $k$-space decomposition of MCAE. Specifically, this can be expressed as

$$MCAE(k) = \sum_i n_{i,k}^{[100]} \epsilon_{i,k} - \sum_i n_{i',k}^{[001]} \epsilon_{i',k}$$

where $k$ is the $k$-point index, $i, i'$ are the band indexes of magnetization direction along [100] and [001], respectively. $n_{i,k}$ is occupation number of this band, $\epsilon_{i,k}$ is the energy of band $i$ at $k$-point $k$.

III. RESULTS AND DISCUSSION

A. MCAE oscillation

Unlike the FM/oxide structure where the MCAE can be accounted as local hybridization of the interfacial Fe-3$d$ orbital and the interfacial O-2$p$ orbital the MCAE of CFA/Ta structure varies strongly when the Ta thickness changes. In this circumstance, MCAE cannot be treated as a local property of the interface. We observe a strong oscillation of MCAE in FeAl-CFA/Ta structure relative to the thickness of capping layer Ta, as shown in Fig. 2. The oscillation period is approximately 4 ML, and the oscillation amplitude decreases as the number of Ta ML increases. This is due to that the confinement effect of QW will become less prominent when the width of QW increases and the bulk states of Ta will account for a larger proportion in all the electron states. Interestingly, the oscillation is smaller in the Co-CFA/Ta structure, the reason for this phenomenon will be discussed later.

To comprehend the origin of the oscillations, we manually tweak the strength of SOC in the structures. Since MCAE only comes from SOC, switching off the SOC of Ta will totally screen out the contribution of Ta to MCAE of the whole system. For the FeAl-CFA/Ta structure, by suppressing the SOC of Ta while still keeping the SOC of CFA, oscillation of the MCAE relative to Ta layer thickness disappears [see cyan lines in Fig. 2]. For the Co-CFA/Ta structure, a smaller oscillation exists and the tweaking of the SOC of Ta has little influence on the MCAE [see red lines in Fig. 2]. These strongly indicate that the electron states in Ta play the determinant role in the MCAE oscillations of CFA/Ta structures.

A further analysis can be carried out by defining the MCAE difference

$$MCAE_{diff}(n) = MCAE(n) - MCAE^{Ta-off}(n)$$

where $n$ is the number of Ta ML, $MCAE^{Ta-off}(n)$ is the result calculated with SOC of Ta switched off. The $MCAE_{diff}(n)$ will only contain MCAE contribution originated from Ta layers, as plotted in the inset of Fig. 2. Note three major differences can be discerned. Firstly, the oscillation magnitude of Co-CFA/Ta vanishes much faster than that of FeAl-CFA/Ta. Secondly, we can define an oscillation period of 4 ML in FeAl-CFA/Ta but it is harder to clearly define an oscillation period for Co-CFA/Ta. Thirdly, in Co-CFA/Ta, the mean value of $MCAE_{diff}(n)$ is essentially zero while the mean value of $MCAE_{diff}(n)$ of FeAl-CFA/Ta largely deviates from zero. The oscillation of physical properties relative to film thickness is a hallmark of QWS, and these three remarkable differences suggest that for FeAl-CFA/Ta, the electron states in Ta layers may form QWS and explain the MCAE oscillation. While for Co-CFA/Ta, since the MCAE oscillation is less prominent, there is less probability to correlate MCAE oscillation with QWS in Ta layers. The subsequent paragraph will concentrate on the analysis of MCAE with special electron states and evidence of the existence of QWS in FeAl-CFA/Ta structure. The same analytic procedures are also applied to Co-CFA/Ta in the Supplemental Material.

B. Critical $k$-points and band structure

Employing $k$-space resolved method, we dissect MCAE into two-dimensional Brillouin zone (2D-BZ) for FeAl-CFA/Ta[9]. Comparing $k$-resolved graphs for structures with different Ta layer thickness, two critical $k$-points, which have large contributions to MCAE, can be se-
selected out, i.e. $k$-points at $[k_x, k_y] = [-0.48, -0.2]$ and $[k_x, k_y] = [0.48, -0.2]$, as shown in Fig. 3 (with number of $k$-points set as $25 \times 25 \times 1$, $k_x$ and $k_y$ ranging from $-0.48$ to $0.48$). The SOC breaks the symmetry of 2D-BZ, contributions to total MCAE slightly differ from each other between these two $k$-points. In fact, when considering the symmetry of the crystal structure, these two $k$-points are identical and locate at the center of $M$ point and $X$ point of the 2D-BZ, and they will be called as critical $k$-point in the following text.

According to second order perturbation theory, the perturbation of SOC to one-electron energies can be written as

$$\delta \epsilon_i = \sum_{i' \neq i} \frac{|\langle i' \rangle H_{SOC} | i \rangle|^2}{\epsilon_i - \epsilon_{i'}} \quad (3)$$

$$P_{corr}^{axis} = \sum_{i} n_i \delta \epsilon_i = \frac{1}{2} \sum_{i} \sum_{i' \neq i} \frac{n_i - n_{i'}}{\epsilon_i - \epsilon_{i'}} |\langle i' \rangle H_{SOC}^{axis} | i \rangle|^2, \quad \text{axis} = [100], [001] \quad (4)$$

where $i, i'$ is the quantum number of one-electron states, $\epsilon_i$ is the one-electron energy and $H_{SOC}$ is the Hamiltonian of SOC, $axis$ is the magnetization direction, and $P_{corr}^{axis}$ is the energy correction to unperturbed state caused by SOC.

This expression indicates that only electron states near Fermi energy have maximal impact on MCAE. To extract out more information about states contributing most to the MCAE oscillation, we systematically examine spin-resolved band structures along different directions at this $k$-point. As an example, we draw the band structure along line $k_y = 2.57k_x + 1.03$, with band index ranging from 209 to 214, as shown in Fig. 4(b) for spin-up electrons, and band 187 to 193 for spin-down electrons, as shown in Fig. 4(d). We find that the spin-up band with index 212 and spin-down band with index 190 traverse Fermi energy along most of the directions in 2D-BZ. As a reminder, this particular number has no physical meaning but only labels the order of Kohn-Sham eigenvalues in the calculation result. Note due to exchange splitting, the energy of spin-down band are higher than the corresponding spin-up band which has identical band index with the spin-up band, so the Fermi-energy-vicinal bands are different for spin-up and spin-down electrons and should be considered separately.

For the Co-CFA/Ta, we find that different from FeAl-CFA/Ta, the rapid variations in 2D-BZ make the ascription of MCAE oscillation to a specific electron state a bit more difficult. We can still select out critical $k$-points but the magnitude of the peak does not have a sharp contrast with other $k$-points, as shown in Fig. S1 of Supplemental Material.
C. Characterization of QWS

To explore the nature of these specific electron states, the band-decomposed charge densities of these Fermi-energy-vicinal states are plotted, and we conclude that these are the quantum well states confined between the FeAl-CFA/Ta interface and the Ta/vacuum surface, as shown in Fig. 5 for spin-up electrons and Fig. 6 for spin-down electrons. Note spin-up electrons of band 209 to 212 are Fermi-energy-vicinal, while for spin-down Fermi-energy-vicinal states, their band indexes are from 188 to 190. For the Fermi-energy-vicinal states of both majority spin and minority spin, i.e. spin-up and spin-down electrons, all of them are mostly confined in Ta layers, as indicated by the orange lines in Fig. 5 and green lines in Fig. 6. With increasing band index, more wave crests are formed, which are the characteristic feature of QWS. The energies of QWS depend on the width of the well, namely, the thickness of the Ta layer. By increasing or decreasing Ta layer thickness, the QWS will fall or rise through Fermi energy, consequently lead to the oscillation of the total MCAE, as suggested by Eq. (4).

**FIG. 5.** Charge densities of energy bands at index (a) 209, (b) 210 and (c) 212. Green color for spin-down electron, orange for spin-up electron and blue for total charge density. The horizontal axes of these figures correspond to the z axis of the crystal structure. Note the energies correspond to the spin-up electrons of these bands are vicinal to Fermi energy, while energies correspond to the spin-down electrons are higher than Fermi energy due to exchange splitting. The spin-up electrons are mostly confined in Ta layers.

For the Co-CFA/Ta structure, the band-decomposed charge densities of Fermi-energy-vicinal states do not perfectly resemble that of an idealized one-dimensional quantum well with infinite potential barriers, the character of QWS is less apparent than FeAl-CFA/Ta. Band-decomposed charge densities of Co-CFA/Ta are plotted in Fig. S3 and Fig. S4 of Supplemental Material.

Before concluding the charge density analysis, we would like to clarify that both Fig. 5 and Fig. 6 are band-decomposed, while the total charge density should be the sum of all the occupied bands. So the crests in the band-decomposed charge densities do not imply a large antiferromagnetic coupling between Ta layers and CFA. The magnetic moments of all the atoms are plotted in Fig. S5 for FeAl-CFA/Ta and S6 for Co-CFA/Ta for the interested reader.

D. Interface potential

The phenomenon that only the FeAl-CFA/Ta structure has strong MCAE oscillation can be understood by the interface potential difference. The potential drop at the interface determines the magnitude of confinement of electrons. Potential of FeAl layer differs substantially from Co layer. As shown in Fig. 7, a larger mismatch of the potential between Ta and FeAl-CFA is found while the mismatch between Ta and Co-CFA is much smoother. Since the constructions of initial structures and the processes of atomic relaxations inevitably lead to a small displacement along z axis between two structures of different interfaces, and the potential difference strongly relies on the origins of coordinates in two structures, we choose part of Ta layers as sampling and minimize the square error so as to accurately align these two structures, i.e.
the potential difference is calculated as

$$V_{\text{diff}}(z) = V_{\text{Co}}(z) - V_{\text{FeAl}}(z + \delta)$$

(5)

where

$$\delta = \arg \min_\epsilon \left\{ \int (V_{\text{Co}}^\text{Ta}(z) - V_{\text{FeAl}}^\text{Ta}(z + \epsilon))^2 dz \right\}$$

(6)

where $z$ is the coordinate along $z$ axis, $\delta$ is the displacement of FeAl-interface structure that accurately aligns two structures, $V_{\text{Co}}$ and $V_{\text{FeAl}}$ are the potentials of Co-CFA/Ta[9] and FeAl-CFA/Ta[9], respectively. $V_{\text{Co}}^\text{Ta}$ and $V_{\text{FeAl}}^\text{Ta}$ are the potentials of Ta layers of Co-CFA/Ta[9] and FeAl-CFA/Ta[9], respectively. $V_{\text{diff}}(z)$ is the potential difference plotted in Fig. 7(c).

FIG. 7. Potentials along crystallographic $z$ direction of (a) Co-CFA/Ta[9] and (b) FeAl-CFA/Ta[9]. (c) Potential difference between Co-CFA/Ta[9] structure and FeAl-CFA/Ta[9] structure, where the upper horizontal axis is for Co-CFA/Ta[9] and the lower horizontal axis is for FeAl-CFA/Ta[9]. The black arrows in (a) and (b) mark the location of the interfaces. The dashed orange and green lines represent $z$ coordinates of each layer in Co-CFA/Ta[9] and FeAl-CFA/Ta[9], respectively. A potential difference of 4.842 eV can be found between two structures at the interfaces.

IV. CONCLUSIONS

By carefully aligning Ta layers of FeAl-interface and Co-interface structures to the same position, little difference is found in Ta part between both structures. But at the interface, the potential is 4.8 eV higher in FeAl-CFA/Ta than Co-CFA/Ta [see Fig. 7(c)]. This larger mismatch ultimately makes confinement effect more prominent in the FeAl-CFA/Ta structure, thus explaining the larger magnitude of MCAE oscillation. The smoother transition of potential in Co-CFA/Ta does not strongly confine electrons into Ta layers, consequently MCAE oscillation relative to Ta layer thickness vanishes faster in the Co-interface structure.

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

2 W. Kang, L. Zhang, J. O. Klein, Y. Zhang, D. Ravelosona, and W. Zhao, IEEE Magn. Lett. 8, 3105805 (2017).

3 S. Peng, W. Kang, M. Wang, K. Cao, X. Zhao, L. Wang, Y. Zhang, Y. Zhou, K. L. Wang, and W. Zhao, IEEE Magn. Lett. 8, 3105805 (2017).

4 H. X. Yang, M. Chshiev, B. Dieny, J. H. Lee, A. Manchon, and K. H. Shin, Phys. Rev. B 84, 054401 (2011).
