Electron Holography of Barrier Structures in Co/ZrAlO$_x$/Co Magnetic Tunnel Junctions

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We investigate the potential profiles and elemental distribution of barriers in Co/ZrAlO$_x$/Co magnetic tunnel junctions (MTJs) using electron holography (EH) and scanning transmission electron microscopy. The MTJ barriers are introduced by oxidizing a bilayer consisting of a uniform 0.45-nm Al layer and a wedge-shaped Zr layer (0-2 nm). From the scanning transmission electron microscopy, AlO$_x$ and ZrO$_x$ layers are mixed together, indicating that compact AlO$_x$ layer cannot be formed in such a bilayer structure of barriers. The EH results reveal that there are no sharp interfaces between the barrier and magnetic electrodes, which may be responsible for a smaller tunnelling magnetoresistance compared with the MTJs of Co/AlO$_x$/Co.

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Recently, much attention has been paid to magnetic tunnel junctions (MTJs) for their fertile physics and potential applications.$^{[1-8]}$ For read head applications of MTJs, both low resistance and high TMR ratio are most important properties. Some results have indicated that an MTJ with a ZrAlO$_x$ barrier, which was fabricated by inserting a Zr layer between Al and the bottom ferromagnetic (FM) electrode before oxidizing, is suitable for the applications.$^{[9,10]}$ However, the tunnelling magnetoresistance (TMR) ratio of ZrAlO$_x$ is much lower than that of the Al$_2$O$_3$ barrier.$^{[9-11]}$

Most recently, transmission electron microscopy (TEM) and off-axis electron holography (EH) have been successfully used in TMJ studies.$^{[12-15]}$ Besides the microstructure information of crystallization, texture, grain size and interfacial roughness obtained from TEM, the barrier potential shape can be directly measured by using EH. In our previous papers,$^{[12,13]}$ the microstructure and the barrier shapes of pure AlO$_x$ barriers ranging from the under-oxidation to the over-oxidation have been reported. In this Letter, the microstructure and barrier elemental distribution of Co/ZrAlO$_x$/Co MTJs has been investigated. The barrier shapes from the under-oxidation to the over-oxidation have also been observed. Compared with the MTJs with pure-AlO$_x$ barriers, the reason for much lower TMR ratio of the MTJs with ZrAlO$_x$ barriers is a bad barrier structure when Zr is inserted.

The MTJ sample for this study was grown by magnetron sputtering deposition on an oxidized silicon substrate with the structure of Ta(5 nm)/FeNi(5 nm)/FeMn(12 nm)/(Co/6 nm)/Al(0.45 nm)/Zr (wedge-shaped 0–2 nm)/(Co/6 nm)/Ta(5 nm) (referred to as Co/ZrAlO$_x$/Co hereafter). The numbers in the parentheses are the layer thickness in nanometers. The oxidation was completed by oxygen plasma exposure. The TMR measurement was held by a conventional dc four-point probe method at room temperature. Cross-section specimens for High resolution electron microscopy (HREM), EH and scanning transmission electron microscopy (STEM) studies were prepared by a standard method including mechanical grinding, dimpling and ion milling. A Philips CM200 FEG TEM equipped with an electrostatic biprism and a Gatan 794 CCD camera and a Philips Tecna F20 TEM were used to characterize the microstructure. Off-axis EH was performed with a biprism voltage of 130–140 V. The holograms were processed using a digital micrograph (DM) software including the Holoworks package.

Figure 1 presents a typical bright-field TEM image of the Co/ZrAlO$_x$/Co MTJ. From a general view of the morphology, the layer of the ZrAlO$_x$ barrier could be identified by the obvious contrast owing to the pronounced atomic scattering parameters. As indicated from this image, the ZrAlO$_x$ barrier layer is continuous and quite flat. Figure 2 shows the high-resolution electron microscopy (HREM) images of the Co/ZrAlO$_x$/Co MTJs with the nominal Zr thickness of 0.4 nm (a) and 1.2 nm (b), respectively. The layer of Ta (capping), Co (top electrode), ZrAlO$_x$, Co (bot-

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tom electrode) have been identified in the micrograph. From the electron diffraction and HREM images we can conclude that the ZrAlO$_x$ barrier layers in the MTJs are with an amorphous structure. The width of the barrier layer could be measured directly from these HREM images and will be discussed in the following.

![Fig. 1. Bright-field TEM image of Co/ZrAlO$_x$/Co MTJ.](image1)

(Fig. 1. Bright-field TEM image of Co/ZrAlO$_x$/Co MTJ.)

![Fig. 2. HREM images of Co/ZrAlO$_x$/Co MTJs with the as-grown Zr thickness of (a) 0.4 nm (over-oxidized barrier), (b) 1.2 nm (under-oxidized barrier).](image2)

(Fig. 2. HREM images of Co/ZrAlO$_x$/Co MTJs with the as-grown Zr thickness of (a) 0.4 nm (over-oxidized barrier), (b) 1.2 nm (under-oxidized barrier).)

Figure 3 shows the TMR ratio versus the thickness $d$ of the as-grown Zr layer at room temperature in the FeNi/Cu/FeNi/FeMn/Co/AlZrO$_x$($d$)/Co/Cu MTJ with a wedge Zr layer oxidized for 90 s. For comparison, the TMR ratio versus the Al-layer thickness in FeNi/Cu/FeNi/FeMn/Co/AlO$_x$($d$)/Co/Cu MTJ (referred to as Co/AlO$_x$/Co hereafter) is also illustrated. It is obvious that the largest TMR ratio of the Co/ZrAlO$_x$/Co MTJ is only about 7\% with the as-grown Zr thickness of 1.02 nm, whereas the largest TMR ratio of the Co/AlO$_x$/Co MTJ is about 28\%.

![Fig. 3. The TMR ratios versus (a) the as-grown thickness of wedge-shaped Zr in the Co/ZrAlO$_x$/Co MTJs oxidized 90 s and (b) the as-grown thickness of wedge-shaped Al in the Co/AlO$_x$/Co MTJs oxidized 90 s.](image3)

(Fig. 3. The TMR ratios versus (a) the as-grown thickness of wedge-shaped Zr in the Co/ZrAlO$_x$/Co MTJs oxidized 90 s and (b) the as-grown thickness of wedge-shaped Al in the Co/AlO$_x$/Co MTJs oxidized 90 s.)

As reported from our previous work,$^{[7,8,16]}$ variation in the oxidation stage of the MTJ with the AlO$_x$ barrier can be reached out by employing a wedge shaped barrier. Along with the different oxidation status of the MTJ barriers from the under-oxidation to the over-oxidation, the corresponding TMR ratio increases with the MTJ-barrier thickness and reaches the maximum value, and then decreases. The optimum oxidation in the MTJ always results in the largest TMR ratio. In the present study, the TMR ratio first increases and reaches the maximum with the increase of the Zr thickness along the Zr wedge. However, it is obvious that the TMR ratio of Co/AlO$_x$/Co MTJs is always much higher than that of Co/ZrAlO$_x$/Co MTJs. Thus, it is still a problem to identify whether the barrier shows the status from the under-oxidation to the over-oxidation.

To understand the above TMR difference, the off-axis electron holography (EH) experiments were carried out to probe the composition gradient and the barrier potential in Co/ZrAlO$_x$/Co MTJs with different Zr thicknesses. Figure 4 shows the averaged phase shift profiles perpendicular to the barrier layer in Co/ZrAlO$_x$/Co MTJs. The local thickness effect of the TEM sample and the magnetostatic contributions to the total phase shift have been eliminated just as our previous work.$^{[12,13]}$ Figure 4(a) shows the phase shift profile of the MTJ with the nominal Zr thickness of 0.4 nm. Figure 4(b) illustrates the phase shift profile of the MTJ with the nominal Zr thickness of 1.0 nm, which corresponds to the largest TMR. Figures 4(c) and 4(d) show the phase shift profiles of the MTJs with the Zr thicknesses of 1.2 nm and 1.5 nm, re-
pectively. The large phase shift from the barrier area near the bottom electrode in Figs. 4(b)–4(d) indicates a higher content of AlOₓ, which coincides with the structure design. Compared to the averaged phase-shift profiles obtained from pure-AlOₓ barriers ranging from the under-oxidation to the over-oxidation in our previous work,[12] we can find that the top and bottom barrier/electrode interfaces of Co/ZrAlOₓ/Co MTJs are all sloped along the whole Zr wedge, which is quite different from the case of the MTJ with pure-AlOₓ barrier.[12] 

![Graphs showing phase shift profiles](image)

**Fig. 4.** Averaged phase shift profiles across the barrier layer in the MTJs with the as-grown Zr thickness of (a) 0.4 nm, (b) 1.0 nm, (c) 1.2 nm (under-oxidized barrier) and (d) 1.5 nm.

![Graph showing elemental distribution](image)

**Fig. 5.** Elemental distribution across the barrier in the MTJ with the as-grown Zr thickness of 1.2 nm. The inset shows the high-angle annular dark-field microscopy image of the scanning position and the arrow shows the orientation of the STEM line scan.

The slopes of the phase-shift curves in Fig. 4 indicate that the top and bottom electrodes are oxidized[12] which could be proven by the width of the oxide barrier. The width of the ZrAlOₓ barrier could be measured from the phase-shift profiles, which is consistent with the results from the HREM images. Here we define the width at the half maximum in the phase-shift profile as the barrier width. From Fig. 4, we can estimate the widths of ZrAlOₓ barriers to be 3.3, 3.7, 3.8, and 4.2 nm with the as-grown Zr thicknesses 0.4, 1.0, 1.2, and 1.5 nm, respectively. However, the thickness expansion from Zr to ZrO₂ is about 2,[8] from Al to Al₂O₃ is about 4/3.[7] For example, for the AlZrOₓ barrier with the as-grown Zr thickness of 1.2 nm and a uniform Al thickness of 0.45 nm, the fully oxidized barrier width is only 3.0 nm, which is smaller than 3.8 nm obtained in the EH experiment. Hence, the ZrAlOₓ barrier width is larger than the fully oxidized barrier width. That is to say, the quality of interface between the AlZrOₓ barrier and the electrodes is bad along the whole wedge. The top and bottom
electrodes of the all MTJs with the ZrAlO$_x$ barrier are oxidized. This may be the reason for lower TMR ratios obtained along the whole wedge in the Co/ZrAlO$_x$/Co MTJs, which also indicates that sharp interfaces are very important to obtain high TMR ratios in MTJs.

The above results also suggest that the oxidation process of the Zr/Al bilayer should be quite different from the pure-Al layer. To clarify further the oxidation process in the Zr/Al bilayer, an STEM line scan has been performed on the Co/ZrAlO$_x$/Co MTJ with a as-grown Zr thickness of 1.2 nm to investigate the elemental contribution in the AlZrO$_x$ barrier. Figure 5 shows the contributions of Zr, Al, and Co elements perpendicular to the barrier layer. The inserted image is a high angle annular dark-field image of the MTJ sample. The arrow shows the orientation of the STEM line scan. Obviously, the AlO$_x$ and ZrO$_x$ layers have mixed together. This is probably because the nominal thickness of the Al layer is only 0.45 nm, which are just two-atom layers of Al. The top and bottom Co layers can be clearly identified. Such small amount of Al can easily diffuse into the Zr layer to form alloys such as AlZr before the oxidation, which indicates that a compact AlO$_x$ layer cannot be formed in such a bilayer structure of baritiers. Since the ZrO$_x$ layer is a much looser oxide compared with the AlO$_x$ layer, the oxygen atoms could oxidize the bottom electrode through the AlZrO$_x$ grain boundaries in the oxidizing process even under the under-oxidization condition, resulting in a much lower TMR ratio.

In conclusion, the barrier potential profiles and the barrier/electrode interface structure in the Co/ZrAlO$_x$/Co MTJs with wedge-shaped barriers have been studied systematically by using the EH technique. It is found that the barrier interface in these MTJs is bad along the whole wedge compared with the ones with pure-AlO$_x$ barriers. The scanning transmission electron microscopy shows that the AlO$_x$ and ZrO$_x$ layers are mixed together. The oxygen atoms could oxidize the bottom electrode through the AlZrO$_x$ grain boundaries in the oxidizing process even in the sample with a much thicker Zr layer, resulting in the tilt interface of the barrier and then in much smaller TMR ratios compared with the MTJs with pure-AlO$_x$ barriers.

References