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# Challenges in the study of Fe/MgO/Fe interfaces using 3D Atom Probe

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ABSTRACT

Detailed interface studies were conducted on two Fe/MgO/Fe systems having different thicknesses of MgO layers, using a laser assisted 3D atom probe. In conjunction with a detailed 3D reconstruction, the system exhibited an additional oxide formation at the interface between MgO and Fe of the multilayer structure. This oxide formation was found to be independent of the laser wavelength, laser fluence and the thickness of the intermediate layers. By using numerical simulations of field evaporation of two layers having two different evaporation fields, we discuss the possible oxidation mechanisms.



## 1. Introduction

Thin films, heterostructures and multilayer structures are increasingly being used in microelectronics and data storage applications. It is well known that the interfacial interactions of these thin films with each other govern the performance and efficiency of the devices. As device sizes keep on decreasing, the study of chemistry of atoms at the interface becomes more and more important for incorporation into next generation devices. Atom Probe Tomography (APT) has emerged as a critical tool for the analysis of multilayered thin films with the main advantages being high spatial resolution and a 3D reconstruction of the atomic structure. Among the modern relevant approaches, APT provides key information in the areas of nanotechnology and device physics due to its uniqueness in three dimensional atomic scale imaging. Earlier, this technique was primarily used to analyse metals and semiconductors but is now also applied to insulators with the advancement of pulsed laser enhanced evaporation [1,2].

Improvement in ultrafast laser assisted field evaporation technology [3,4], allows us to analyse materials with low conductivity [5] as well as have a good 3D atom probe reconstruction for high band gap materials. Some examples include materials like $Al_2O_3$ [6], $HfO_2$ [7], $Fe_2O_3$ [8], $CeO_2$ [9] and even MgO, by APT [10–14]. A more recent APT study on wide bandgap semiconductors and nanostructures has been recently carried out by Lorenzo et al. [15]. APT studies were initially limited to needle shaped structures, but with the advent of Focussed Ion Beam (FIB) milling technology and lift out technique [16], they have advanced to a wider spectrum of samples which can be processed into tip like structures and subsequently analysed. APT studies on a wide variety of materials are now possible including semiconducting and insulating thin films for various applications in magnetic junction transistors, silicon field effect transistors and solar technologies, to name a few [17].

Oxides, sandwiched between metal layers are widely used in magnetoresistance devices [18] and superconducting devices [19,20]. Analysis of the interface with reference to elemental segregation at the boundaries is the key to understanding and improving performances in these devices. However, the field difference during field evaporation during transition from a highly conducting (metallic) interface to a poorly conducting (insulator) interface and again back into the metallic interface gives rise to a new set of challenges in the field of APT analysis. Detailed information related to elemental boundary conditions is one of the critically limiting tasks for the improvements in the performance of Metal/Insulator/Metal systems like Fe/MgO/Fe. Some work on the interface properties of similar heterostructure materials like FeCoB/MgO/FeCo and CoFe/MgO/CoFe have been carried out by Marquis and Larson respectively [21,3].

Although various groups have investigated by means of simulation, the interface between Fe/MgO using first principle calculations [22,23], these are all based on assumptions and ideal sample conditions. The actual interface study obtained using methods like Reflection High

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Energy Electron Diffraction [24,25] and X-Ray Photoelectron Spectroscopy [25] gives two dimensional information for the interface area. Transmission Electron Microscopy (TEM) Electron Energy Loss Spectroscopy also provides an indication of the interface abruptness and the absence of the oxide layer [26] but getting an accurate three dimensional picture of the atom distribution and the interface is very challenging as TEM has a much larger field of view making it difficult to have the measurement of concentrations less than 1 at.% [27]. For obtaining accurate 3D information regarding elemental data, as well as their distribution, it is essential to use a technique like atom probe to accurately analyse these interfaces.

It was recently proven that the use of comparatively lower wavelengths (UV range) in the laser assisted APT gave rise to better signal to noise ratio and hence better APT performances [28]. In the case of Fe/MgO/Fe structures, the influence of the laser wavelength on the performances of APT in terms of mass resolution was already discussed by the authors [11]. However, concerning the study of the interfaces, Moutanabbir et al. [29] recently asserted an improvement of the image of $Si^{28}$ and $Si^{30}$ interfaces using UV light in place of visible light. In the case of FeCoB/FeCo/MgO/FeCo/IrMn multilayer, Marquis et al. [21] has systematically studied the evolution of the tip shape by TEM at different stages of evaporation which was correlated to the induced artefacts. These artefacts might be one of the reasons for the formation of an interfacial oxide layer. Apart from that, the authors speculate the reasons of layer formation to be adsorption (and subsequent field evaporation) of residual vacuum gases or the preferential diffusion of electronegative oxygen away from the field evaporated surface subsequent to a field evaporation event that resulted from evaporation of Mg prior to oxygen. Authors only analysed a single thin layer of MgO (~2.7 nm) with single wavelength (532 nm) and observed the formation of interfacial oxide layer. However in the study presented here we have additionally investigated the influence of both the thickness of MgO layer (4 nm and 32 nm) and the influence of two different laser wavelengths (green and UV), which we believe is necessary to confirm the formation of the interfacial oxide layer. In this work, we have comparatively studied the interface between metallic layer Fe and insulating layer MgO using two different laser wavelengths, particularly, UV (395 nm) and green (515 nm). Moreover, the formation of the oxide layer, at the lower interface was studied by changing the laser contribution to evaporation. The mechanisms for field evaporation of oxides have been discussed in a previous publication [30].

## 2. Experimental methods

### 2.1. Deposition of MgO layer

The multilayered structures of Fe/MgO/Fe were prepared by means of argon plasma sputter deposition on a prepatterned substrate consisting of an assembly of flat-topped Si (100) pillars ($5 \times 5 \times 100\ \mu m^3$). Prior to deposition, the substrate was cleaned for 10–15 min in a standard solution of $H_2O_2 + H_2SO_4$ and after that were cleaned in another solution of 10% HF for 10 min to remove residual contamination and silicon oxide. These were then thoroughly rinsed with distilled water and dried in a stream of dry nitrogen. Afterwards, the layers to be investigated were deposited within the sputter deposition chamber. The schematic of the sputter deposition setup used is as mentioned in literature [31]. It was very important to clean the substrate by ion beam prior to deposition to achieve good mechanical stability of the specimen [31]. The base pressure of the deposition chamber prior to deposition was $10^{-5}$ Pa. The substrate and target cleaning was done with 500 V $Ar^+$ ions and a beam current of 15 mA for 20 s. Ar pressure of the system during sputtering was $2 \times 10^{-2}$ Pa. The MgO layer was deposited using an MgO target with no further additional oxidation. The sputtering rate for Fe and MgO were 2.26 and 0.3 nm/min respectively. The first and third deposited Fe layers were of 30 nm thickness. The insulating barrier of MgO was deposited with a thickness of 4 nm on the first set of sample and 32 nm on the second set.

### 2.2. Tip preparation and measurement

Silicon pillars were removed from the wafer and mounted on a fine tungsten needle under an optical microscope using a fine micromanipulator and conductive commercial adhesive. These were then subjected to Focussed Ion Beam (FIB) milling and shaped into tips suitable for APT analysis by means of an optimised technique. To avoid damages in the region of interest and reduce Ga implantation, the multilayer was capped with a Cr layer of 500–600 nm prior to exposure to the Ga beam [32]. Fig. 1a and b shows the Scanning Electron Microscopy (SEM) image of the specimen with different thicknesses of MgO layer prior to analysis. These images confirm a geometrically appropriate APT tip with dark and light contrast indicating different surface charges between the conducting and insulating materials. The comparatively dark Fe and light MgO layers are clearly seen in the image. The specimen of Fig. 1a has two trilayer stacks of Fe/MgO/Fe separated by a gold layer of 10 nm thickness. The exact thickness of the layers cannot be accurately determined in SEM and are very close to the expected thickness. Sample thicknesses were calculated according to the deposition rates within the sputter deposition chamber as mentioned in the previous section. These multilayers were analysed by Laser Assisted Wide Angle Tomographic Atom Probe (LAWATAP) in an ultrahigh vacuum chamber at a pressure of $10^{-7}$–$10^{-8}$ Pa. Details of the instrument are as given in literature [33]. The femtosecond laser pulse system used was an amplified ytterbium-doped laser (AMPLITUDE SYSTEM HR-pulse) with a pulse length of 350 fs and the repetition rate of 100 KHz. The laser system is equipped with three different wavelength sources, infrared (1030 nm), green (515 nm) and ultraviolet (343 nm). For our work, green (515 nm) and UV laser (343 nm) are used. The detection rate for all tip samples was fixed at 0.005–0.003 atoms/pulse throughout the experiment. Prior to analysis, all the sample tips were cooled down to 80 K.

## 3. Results and discussion

### 3.1. Analysis of 4 nm MgO layer

Ultraviolet laser ($\lambda_1 = 343$ nm): Analysis of the sample containing a 4 nm thick MgO barrier was performed using ultraviolet laser. Analyses were performed using a laser fluence of 4 J/m$^2$ focused at the apex of the specimen throughout the experiment. The mass spectrum of the thin MgO layer analysed within UV range is shown in Fig. 2a. The mass spectrum reveals the expected peaks for single and double charged Mg at ~24 amu and ~12 amu, the peaks of single and double charged Fe at 56 amu and 28 amu, $O_2$ at 32 amu and O at 16 amu. A rigorous scrutiny reveals the presence of molecular ions of Mg–O bonds in the analysis. In addition, the mass spectrum in the proximity of the barrier shows several metallic oxide peaks, such as $FeO^+$ and $Fe_2O$. Also, a few hydrogen and oxygen peaks are observed from the residual gases like $H_2$ and $H_2O$ in all probability adsorbed from the vacuum preparation or analysis chambers.

To study the interface for the 4 nm thick MgO layer, the concentration profile was calculated on a parallelepiped volume of $7 \times 7 \times 40$ nm$^3$ indicated by red lines in Fig. 2b. In this sample (4 nm), a high purity ($\approx$90%) of Fe concentration is found in the top layer. The Mg and O concentrations show maxima of 44% and 42% respectively. A ratio of $1.04 \pm 0.15$ between Mg and O is detected in the centre of the oxide barrier as shown in Fig. 2c. The O peak is extended to the right of Mg peak suggesting oxidation of the bottom interface [6,28]. The presence of the molecular species of FeO and $Fe_2O$ is higher in the bottom interface. There is a small Fe peak immediately after the MgO layer but is not coinciding with the O peak.