Evolution of magnetic and structural properties of MgO thin film with vacuum annealing

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Abstract: In this work, investigation of MgO thin film, deposited via e-beam evaporation is carried out with increasing annealing temperature. Structural properties, as elucidated using X-ray based techniques viz. grazing incidence XRD and X-ray reflectivity were associated with magnetic properties of film as observed using superconducting quantum interference device (SQUID) magnetometer. As-deposited film is polycrystalline in nature and exhibits ferromagnetism, which is attributed to presence of Mg vacancies. Vacuum annealing results densification of film with concurrent increase in electron density and reduction in film thickness and saturation magnetization. However, at sufficiently high temperature, electron density and saturation magnetization decreases comparative to as-deposited film. The results are significant for the optimization of desired functional properties of MgO particularly in MgO based magnetic tunnel junctions, providing high tunnel magnetoresistance ratio.

Keywords: MgO film, annealing, SQUID, XRR

1. Introduction

The increasing miniaturization of devices induces the requirement of detailed exploration of thin films and multilayers, which exhibit various important and interesting phenomenon like giant magnetoresistance (GMR), exchange bias, tunnel magnetoresistance (TMR), spring effect etc. The magnetoresistance observed in conventional AlO, barrier based MTJs, was not sufficient for spintronic applications. Moreover, the observation of GMR leads to potential spin transport applications for only two decades. However, relatively larger magnetoresistance and negligible temperature dependence for...
MgO based magnetic tunnel junctions triggered investigations of global scientific community in this direction.

Good quality MgO film is important for developing efficient magnetic tunnel junctions (MTJs) having potential applications in magnetic sensors [1], spin logic devices [2], magnetoresistive random access memory (MRAM) [3], read heads for disk drives [4] etc. In fact recent developments by Chen et al., show the applications in wearable medical devices by developing flexible MgO barrier MTJs on ultra-thin Silicon membrane [5]. The high melting temperature, high thermal conductivity, compatibility with reactor materials and small absorption cross-section of thermal neutrons makes MgO potential candidate for wide range of applications [6].

Theoretical predictions and experimental confirmations reveal that MgO film as tunnel barrier in MTJs play an important role in realizing giant tunnel magnetoresistance [7]. In fact, an epitaxial MTJ with crystalline MgO barrier, exhibits coherent tunneling of $\Delta_1$ majority states resulting in large tunnel magnetoresistance ratio [8]. Perpendicular magnetic anisotropy (PMA) exhibit emerging applications in high-density magnetic recording media [9] was also evidenced at the interface of ferromagnetic (FM) film with MgO [10, 11] and it was observed that MgO capping can increase PMA [10]. Such enhancement in PMA is a result of hybridization of 3d orbitals of FM with O-2p orbitals [12], which depends further on the quality and structure of deposited MgO films. Extensive studies on optical, electrical and structural properties of MgO film prepared by various methods like sol-gel method, ion beam sputtering, pulsed laser deposition etc. have already been carried out in literature.

However, any sort of ferromagnetism in MgO, also referred as d0 magnetism, because of structural defects, may affect the spin transport properties and is an active and unclear topic of current interest. Till date, CoFeB/MgO based MTJs provides a giant TMR ratio at room temperature [13]. Post deposition annealing results in formation of bcc structure of magnetic electrode in TMR multilayer at below 773 K. Therefore, investigation of structural and induced magnetic properties of MgO film with annealing temperature is also important. In this work, structural properties of MgO film is studied using X-ray based techniques viz. X-ray reflectivity; X-ray Diffraction, while magnetic properties are elucidated using superconducting quantum interference device (SQUID) magnetometry.

2. Experimental

MgO powder with 99.99% purity was used to prepare pellets, which were sintered at 1473 K for 12 h for densification. These pellets were loaded in ultra-high vacuum chamber with electron beam evaporation setup to carry out deposition of MgO film on polished Si (100) substrate. Base vacuum prior to deposition was 7 x 10^{-8} mbar, which reduces to 1 x 10^{-6} mbar during deposition. Deposition rate was maintained 6Å / min. Structural parameters of the samples- like roughness, electron density and film thickness are investigated using X-ray reflectivity (XRR), done using Bruker D8 Advance Diffractometer with a Göbel mirror to generate a monochromatic parallel beam of Cu Kα radiation (wavelength, $\lambda$= 1.54 Å). Crystalline quality of deposited film was examined using GIXRD measurements done on the same diffractometer. Post deposition sample annealing at various temperatures were done ex-situ in an evacuated chamber with base vacuum of 1x10^{-6} mbar. Magnetic properties of as-deposited and annealed MgO films are investigated at 300 K using a SQUID magnetometer (Quantum Design).
3. Results and Discussion

Figure 1. X-ray reflectivity of MgO film at 300 K, 523 K and 623 K. Continuous solid curves characterizes the best possible fit of experimental data. For easy viewing curves are shifted vertically relative to each other. Inset show the electronic scattering length density profiles as function of z (depth)

Figure 1 shows the XRR of MgO film annealed at various temperatures. The data was fitted with Parratt formalism [14]. Electron density profiles is shown in inset of figure as function of increasing z (depth) from air. Figure 2(a) shows the variation of MgO film thickness as calculated from fitting of X-ray reflectivity data, as function of annealing temperature. The as-deposited MgO film exhibits thickness of 62 nm, which reduces to 60 nm and 54 nm for annealing at 523 K and 623 K respectively. With further increase in annealing temperature, film thickness becomes constant. Such reduction in thickness of thin film has also been reported in previous studies for oxide films, which is attributed to film densification [15].

Figure 2. (a) MgO film thickness observed from XRR fitting as function of annealing temperature (b) Fitted XRR in small q-range about critical angle. Dashed line show the qc values, where intensity reduces to half. (c) Variation of electron density as reported from fitting of XRR data in small q-range.
Figure 2b shows the fitted XRR data in small q range about the critical angle region at various temperatures. The dashed line (vertical) intersects the XRR data at point (critical angle), where reflected intensity reduces to half of the initial value. One may note that annealing till 623 K, results in shift of critical angle to higher value relative to as-deposited specimen indicating an increase of electron density and hence mass density. The concurrent increase of mass density and reduction in film thickness with the vacuum annealing has also been reported in previous studies [16, 17]. However, with further increase in annealing temperature at 823 K, critical angle shifts to lower value.

The variation of electron density as calculated from fitting of XRR data, with annealing temperature is shown in Figure 2 (c). Electron density of as-deposited MgO film is observed as 2.97 E-03 ± 2.0 E-05 nm$^2$, which is near to bulk value of 3.04 E-03 nm$^2$. With thermal annealing till 623 K, electron density and hence mass density increases to theoretical value signalling film densification because of elimination of defects, vacancies and stresses in as-deposited thin film. The results are in agreement with thickness modification of MgO film with annealing temperature.

The crystallinity of MgO film was explored via X-ray diffraction in grazing incidence mode (GIXRD). Figure 3 gives the GIXRD spectrum of as-deposited MgO thin film with incident angle fixed at 0.5 degree. The polycrystalline nature of MgO film was observed with all the peaks attributed to MgO, confirming the absence of any impurity phases.

Figure 3 shows the M-H curves (M = magnetization, H = applied magnetic field) measured at 300 K, for MgO film annealed at various temperatures, after subtracting the signal from Silicon substrate. One may note that as-deposited film exhibits ferromagnetism. Such appearance of hysteresis loop has also
been observed in earlier studies [18-21]. Theoretical calculations and experimental confirmation suggest that, magnetism in MgO film is driven by Mg vacancies, which induces spin polarization of 2p electrons of surrounded Oxygen atoms. [18, 19]. However, certain reports suggest that oxygen vacancies and hydrogen, adsorbed at oxygen vacancies may add to room temperature ferromagnetism [22]. For the present case, as deposited MgO film exhibits saturation magnetization of $M_s \approx 15 \text{ emu/cm}^3$, which reduces further with vacuum annealing. It is important here to note that MgO being hygroscopic is vulnerable to form diamagnetic Mg(OH)$_2$, which further reduces ferromagnetic ordering [22]. Vacuum annealing is also expected to increase the number of oxygen vacancies, which may degrade ferromagnetism [19, 23]. The variation of saturation magnetization with the annealing temperature is presented in inset of Figure 4. One may note that with increasing annealing temperature, $M_s$ reduces significantly below 5 emu/cm$^3$ and beyond 523 K decreases slowly. In a study by Li et al., it was also observed that crystallinity of MgO film enhances with annealing in oxygen and vacuum environment, accompanied with reduction of Mg vacancies. However, there is relatively higher reduction in $M_s$ for vacuum annealing relative to oxygen annealing [19]. Therefore, such lowering in saturation magnetization with annealing for MgO can be understood as result of all possible competing contributions discussed here.

4. Conclusions

Structural and magnetic properties of MgO film as function of annealing temperatures have been investigated. As-deposited film was polycrystalline with relatively low electron density, because of presence of defects and vacancies, which results in appearance of ferromagnetism. Vacuum annealing results in film thickness reduction and increase of electron density accompanied with removal of defects and voids, which also lead to increase in crystallinity. The removal of vacancies (Mg) results in lowering of saturation magnetization. However, at sufficiently high temperature, electron density reduces
concurrently with reduction of saturation magnetization. The results are important in view of spin-transport applications, where optimization of structural and magnetic properties of MgO are needed for achieving a high value of spin-polarized current across the junction.

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