



Dissolution behavior of MgO thin film-barrier magnetic tunneling junctions

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Abstract

The reaction between the water and the MgO thin film of the magnetic tunneling junction barrier under different temperatures were investigated. The epitaxial MgO (001) thin film with a thickness of 20 nm was exposed to the deionized water for 5 min at different water temperatures. X-ray photoelectron spectroscopy (XPS) combination with in situ Ar⁺ ion etching and scanning electron microscope (SEM) was used to investigate the chemical composition and formation of the Mg(OH)₂ layer on the MgO film. SEM results showed that the surface morphology strongly depended on the temperature. XPS depth profile measurements reveal the effect of the water temperature on the dissolution of MgO film. The remaining thickness of the film decreases with increasing water temperature. This work proposes the qualitative model representing the mechanism dissolution behavior and the formation of Mg(OH)₂ layer on the MgO film under different water temperatures.

1 Introduction

Magnetic tunneling junctions (MTJs) is the heart of the spintronic devices which are widely used in numerous applications including magnetic random-access memory (MRAM) and the read head sensors of hard disk drives (HDDs) [1–3] because they can detect miniature magnetic field variations with a high spatial resolution [4]. The MTJs consists with two layers of ferromagnetic separated by insulating layer (See Fig. 1) [5]. It is known that crystalline MgO (001) thin film is nowadays used as the insulating barrier layer in the MTJs instead of the previous amorphous Al₂O₃ barrier due to it can enhance tunneling magnetoresistance (TMR) value in the MTJs from 70 to 600% at room temperature [5–8].

Several researchers point out that high sensitivities of the MTJs are a result of the huge TMR ratio which depends on the thickness and texture of the MgO insulating barrier layer [1–3, 5, 7]. Practically, in MTJs fabrication processes, the thin films are exposed to deionized water and moisture. Unfortunately, the thickness of MgO insulating layer can be reduced during this process because of its high solubility [9]. Moreover, MgO can easily absorb moisture and develop a thin Mg(OH)₂ layer, on its surface; this leads to the formation of several defects/impurities within the MgO barrier layer [10, 11]. Nagamine et al., [12, 13] found that the moisture from the film deposition system was the cause of the formation of several defects/impurities within the MgO barrier layer. In addition, Kuenzel et al. [14] suggested that the hydrated surface layer can be dissolved in the water when a higher relative humidity or a significant amount of the water presented. This results in the reduction of the thickness of the MgO barrier layer and forming the Mg(OH)₂ layer, hence the degradation of MTJs. Consequently, the performance of the spintronic devices such as the read head sensors of hard disk drives significantly drops. Therefore, understanding the interaction mechanism between water, temperature and MgO film is the essential knowledge to prevent the damage of MgO thin film layer. Herein, the mechanism of MgO dissolution and the effect of temperature on dissolution behavior is reported. The qualitative model of dissolution behavior of MgO is also proposed.

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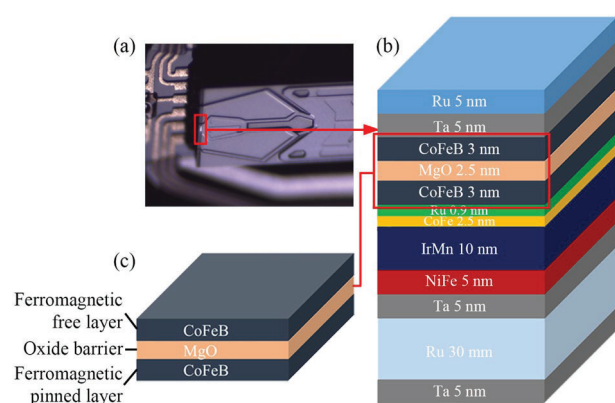


Fig. 1 **a** and **b** Read head sensor of hard disk drives (HDDs) and **c** The MgO tunnel barrier in magnetic tunneling junctions (MTJs) structure (Reproduced with permission from Refs. [15, 16])

2 Experimental

2.1 Sample preparation

To obtain the results that can be applied to the assembly processes of the magnetic sensors of HDDs, the experimental conditions were designed according to the real environment of the processes. The dissolution behavior of the MgO thin film was investigated under different temperatures. The commercial epitaxial MgO (001) thin films (obtained from Western Digital (Fremont), LLC, Fremont, CA, US) with 20 nm thickness on the Si substrate from the same production lot were cut into $1 \times 1 \text{ cm}^2$ square shape using a diamond scribe. The 1 ml of droplets of the deionized water with six different temperatures (0, 10, 20, 25, 50, and 75 °C) was dropped on the top of the film surfaces for 5 min. After that, the droplet of deionized water was removed from the film surfaces by N_2 blower. The samples are denoted as MgO-0, MgO-10, MgO-20, MgO-25, MgO-50, and MgO-75 representing water temperatures.

2.2 Characterization

In this experiment, the remaining thickness of the film after dissolution is approximately a few nanometers; therefore, XPS depth profile measurement method is selected to determine the remaining thickness due to its high surface-sensitive analytical capability which is suitable for extra thin films. The integration of XPS (the PHI 500 Versaprobe-II) and in situ Ar^+ ion bombardment was used to examine the remaining thickness and the depth distribution of the chemical composition of the films. This instrument uses a monochromatic Al-K_α (1486.6 eV) X-ray source. The in situ Ar^+ ion bombardment with 1 keV energy and

a beam size of $2 \times 2 \text{ mm}^2$ were proceeded using an ion gun in the analysis chamber. All spectra ($\text{Mg}2p$, $\text{O}1s$, $\text{C}1s$, $\text{Si}2p$) were collected using the same pass energy of 23.5 eV except the $\text{O}1s$ spectra of MgO-25, MgO-50 and MgO 75 which were collected at 11.75 eV of pass energy. Corrections of the energy shift due to the steady-state charging effect of the samples were carried out by reference to the $\text{Ar}2p$ spectra at 243 eV [17]. The atomic concentrations were calculated from the $\text{C}1s$, $\text{O}1s$, $\text{Mg}2p$ and $\text{Si}2p$ photoelectron peak intensity using Shirley background subtraction and sensitivity factors provided by the OPERATOR'S PHI MultiPak™ Software Manual [18].

3 Results and discussion

3.1 Surface morphology

The microstructure of the MgO thin film surfaces after being exposed to different water temperatures are carried out by scanning electron microscope (SEM). The SEM micrographs as shown in Fig. 2, illustrate the change of morphology of the dissolved areas and vicinities. It is found that the clusters of new layers form over the surfaces in every condition. Significantly, the number of clusters of new layers take place and increase with increasing water temperature. These new layers could be caused by the chemical reaction between the deionized water and MgO film. Moreover, the reaction could also be accelerated by the temperature of the water. Influence of water temperature on dissolution behavior is indicated by the remaining thickness of the film after being exposed by the water.

3.2 Remaining thickness of the films

A plot of the atomic concentration percentage of elements as a function of sputtering time of the fresh MgO thin film and the films after dissolution are exhibited in Figs. 3 and 4a, respectively. As mentioned above, the $\text{O}1s$ spectra of the MgO-25, MgO-50 and MgO-75 were collected using 11.75 eV of pass energy. Using lower pass energy is result in the lower $\text{O}1s$ atomic concentration. However, it does not affect the variation of the film depth profile. From Fig. 3, the depth profile of the pristine sample shows that the $\text{C}1s$ signal due to the natural contamination is detected on the top of the film surfaces. After the first sputtering cycle of in situ Ar^+ ion, the carbon contamination is removed and the concentration of the $\text{Mg}2p$ and $\text{O}1s$ are continuously constant at 50% of the atomic concentration. Then, after being sputtered deeper into the film, the $\text{Mg}2p$ and $\text{O}1s$ concentrations start decreasing meanwhile the signal of $\text{Si}2p$ increases. The intersection point between the $\text{Mg}2p$ and $\text{Si}2p$ lines may be indicated that the interface region between MgO thin film

Fig. 2 The SEM image of the MgO thin film morphology after exposed to deionized water. (Magnification: $\times 5000$)

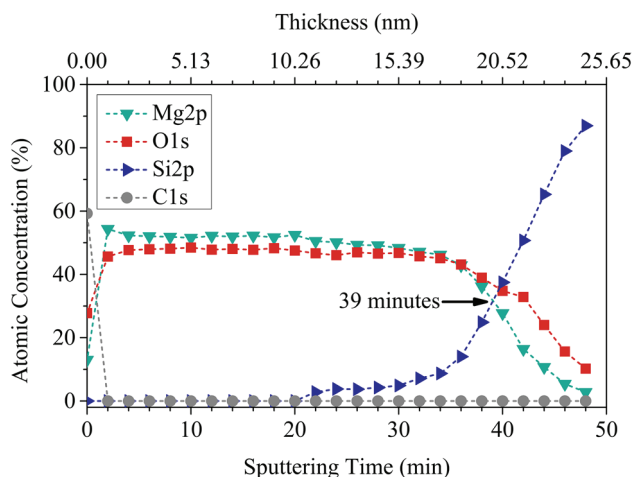
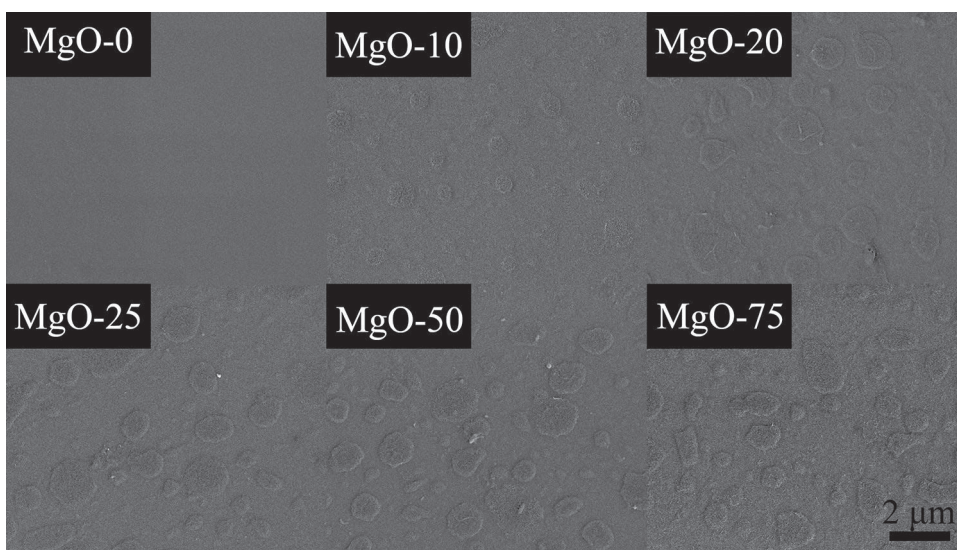


Fig. 3 The XPS depth profile of the 20 nm MgO thin film. The black arrow indicates the reference point of the remaining thickness

and Si substrate are reached after sputtering through the film. The variation of atomic concentration as a function of the sputtering time elucidates the changes of the film chemical composition along the depth. Moreover, it can be used to investigate the thickness of the film. By employing the depth profile measurement shown in Fig. 3, the point that the Si2p line intersects with the Mg2p line is used as the reference point (at 39 min, indicated by the black arrows) to determine the remaining thickness of the films by comparing with the sputtering rate of the fresh MgO thin film, which is approximately 0.513 nm/min (i.e. sputtering rate = thickness of the film/sputtering time).

When considering all dissolution conditions as shown in Fig. 4a, the XPS results reveal the effect of temperature in the reduction of the film thickness. The thickness decreases with the increase of water temperature. This is because the

dissolution rate of the MgO thin films strongly depends on the water temperature. These results are in agreement with the previous work reported by Bharadwaj et al. [19], who demonstrated that the dissolution rate dramatically increased with increasing temperature. Furthermore, M. Komiyama et al. [20], also pointed out that the MgO can be hardly dissolved in a cold water. These could be the reasons why the remaining thickness of the MgO-0 sample is thicker than that of the MgO-75 sample.

To verify the remaining thickness of the MgO thin film after being exposed to deionized water, the cross-section of the film was investigated by using Focus Ion Beam (FIB) with gallium (Ga) ion milling. The cross-sectional of the film is photographed at a take-off angle of 52° using SEM.

The FIB-SEM cross-sectional images are illustrated in Fig. 4b. The different contrast in the images is referred to the different morphologies of the film and substrate. The darker area represents the substrate region while the brighter area is the film region. The results show that the film thickness decreases with the increase of the water temperature exposed. This is in a line with the XPS depth profile results, as discussed above.

3.3 Depth profiling of the films

To identify the chemical state of elements on the films after dissolution, the XPS spectra of all elements are recorded and deconvoluted with a combination of Gaussian (70%) and Lorentzian (30%) fits. The deconvoluted high-resolution O1s core level spectrum of the representative sample (MgO-0, MgO-25 and MgO-75) at the selected sputtering time (0, 2, 10, 20 and 30 min of sputtering time) are demonstrated in Fig. 5a–c. The intensity of O1s spectra of the MgO-25 and MgO-75 samples are lower than those of MgO-0 sample because the lower pass energy used. Before

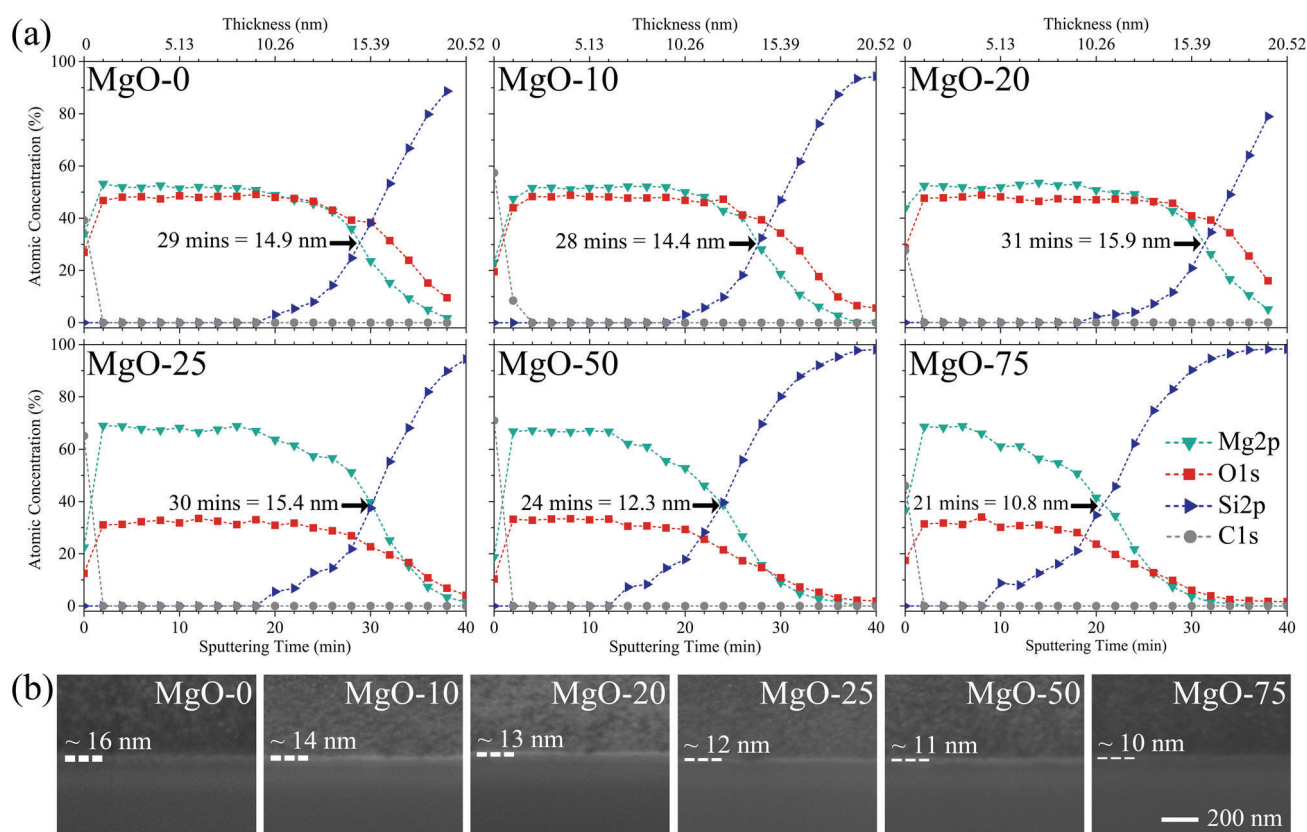


Fig. 4 **a** A plot of atomic concentration percentage as a function of sputtering time of the MgO thin films after dissolution, **b** the FIB-SEM cross-sectional of the MgO thin film at different water temperatures. (Magnification: $\times 100K$)

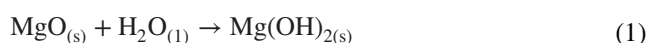
the bombardment of Ar^+ ion, the O1s spectra are deconvoluted into three subpeaks at the binding energy of 530.3, 532.1, 532.8 eV which correspond to the binding energy of O–Mg, O–C and O–OH, respectively. The presence of the OH group represented by O–OH peak in the deconvoluted O1s spectra, as shown in Fig. 5a–c, confirms that the film reacts with the deionized water and creates the $Mg(OH)_2$ layer over their surface. This result corresponds to the formation of the new layer over the film surface observed by the SEM, as shown in Fig. 2. After 2 min of sputtering, the peak position shifts 0.1–0.2 eV to the lower binding energy while the O–C subpeak is eliminated and the intensity of the O–Mg subpeak dramatically increases. At the same time, O-vacancy identified as the oxygen deficiency takes place at 530.6 eV of the binding energy and decreases with the sputtering time. The oxygen deficiency could be caused by the in situ Ar^+ ion sputtering that removes the oxygen atom from the lattice MgO. Then, after sputtering to the further depth, the O–Si subpeak appears at the binding energy of 533 eV meanwhile the intensity of another subpeak start decreasing.

To quantify the amount of the $Mg(OH)_2$ which forms over the film surface, the maximum intensity of O–OH subpeak of all sample is converted to the atomic concentration

percentages and established in Fig. 5d. The results suggest that the O–OH concentrations continuously decrease with increasing sputtering time. This implies that the $Mg(OH)_2$ permeates into the deeper layer of the film. Significantly, the amount of $Mg(OH)_2$ in the films increases with the water temperature.

3.4 Dissolution mechanism of the films after being exposed to deionized water under different temperatures

To understand the effect of the temperature on the dissolution behavior of the film, a schematic drawing of the dissolution mechanism of the MgO thin film is illustrated in Fig. 6. After the films are exposed to the deionized water, the water molecules are rapidly absorbed on the film surface and infiltrate into the deeper layer of the film. Then, the chemical composition of the film which reacted with water is transforming into the $Mg(OH)_2$ (as confirmed by the XPS results). This can be expressed as the Eq. (1) [21]:



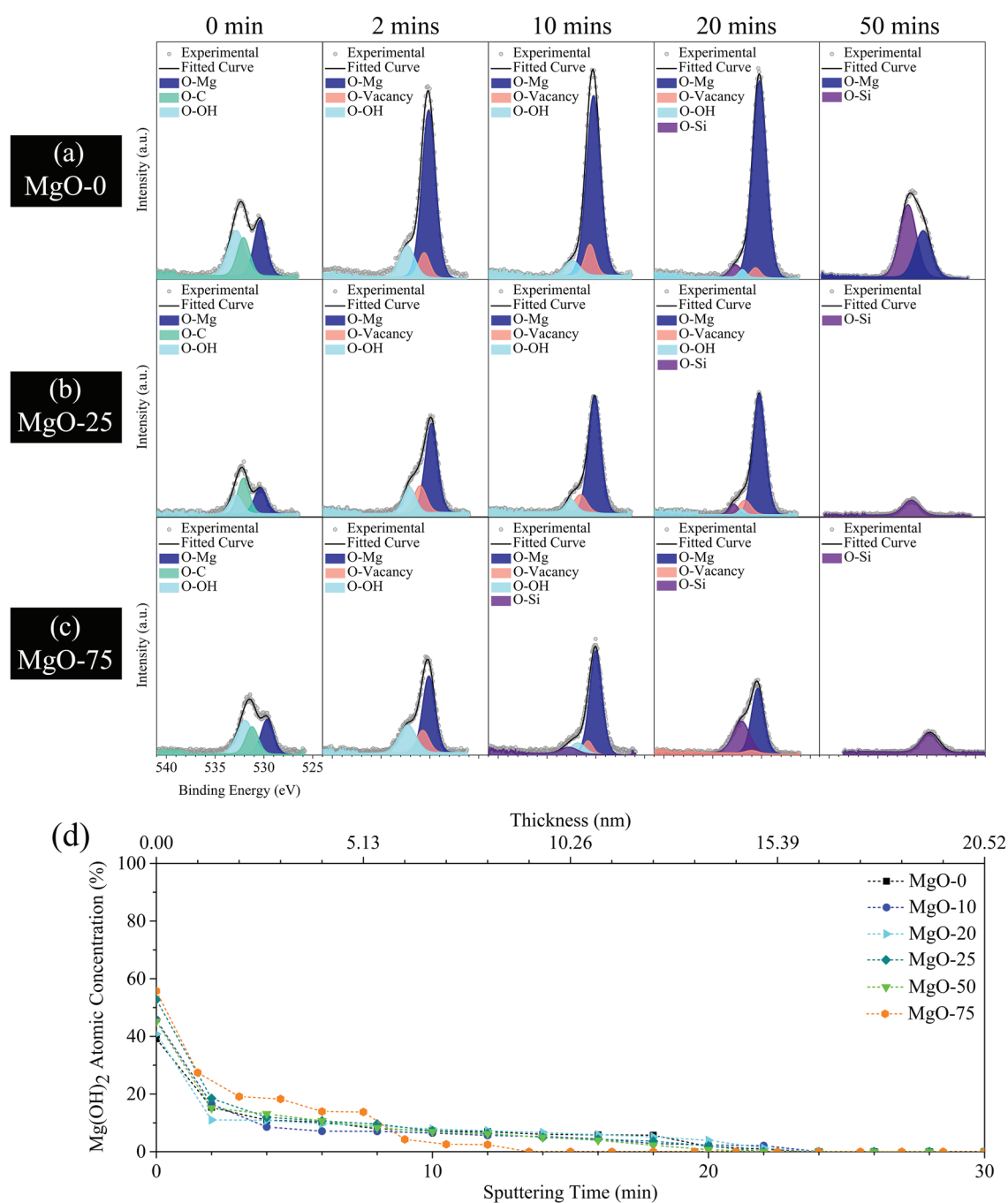
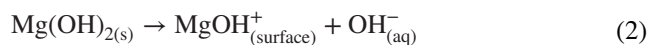


Fig. 5 **a–c** the deconvoluted O1s spectra of the MgO-25 sample at different selected sputtering time, **d** a plot of the atomic concentration of Mg(OH)₂ of each sample

Subsequently, the hydroxide layer is partially releasing OH[−] ions into the deionized water and creating MgOH⁺ on the film surface expressed as the Eq. (2) [21–23]. This is evidenced by a change of the film morphology as manifested in the SEM micrographs (Fig. 2).



The Mg²⁺ and OH[−] are continuously released from the film surface. Consequently, the morphology, thickness, and chemical composition are finally changed. At the higher temperature, the required activation energy is less than that of the lower temperature as illustrated in Fig. 6(top diagram). Moreover, the increase of water temperature enhances the

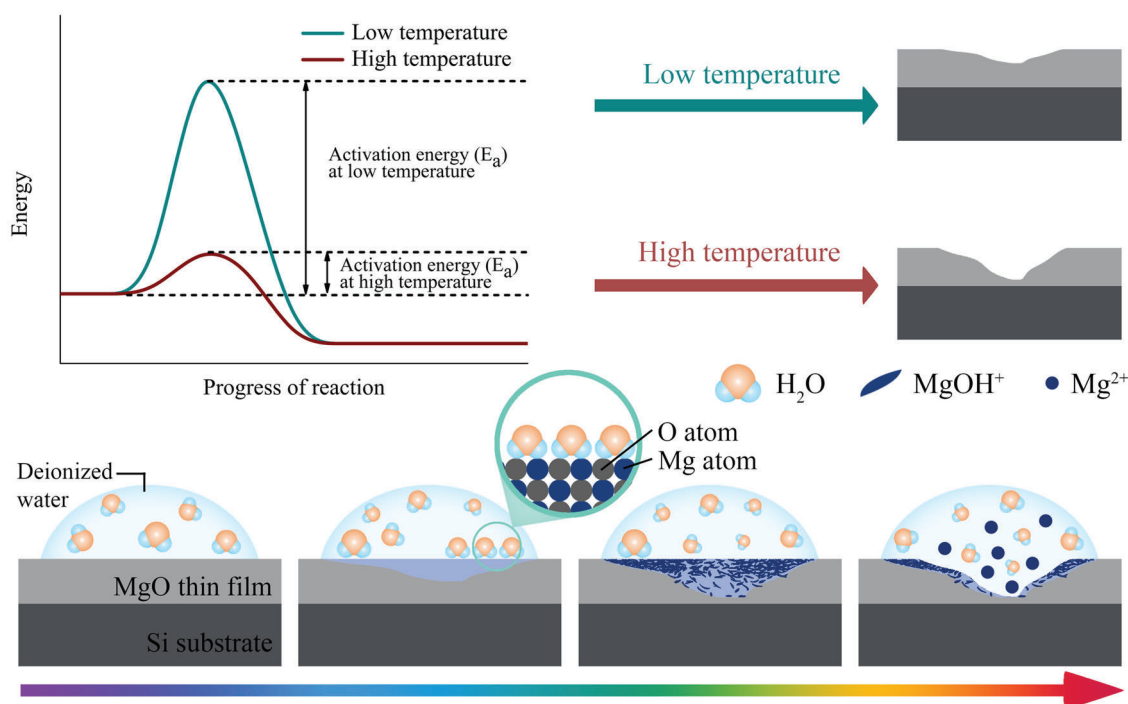


Fig. 6 The dissolution model of the MgO thin film after being exposed to deionized water

kinetic energy of the molecules of water. Therefore, the probability of water molecules interacts with the MgO film is greater in high temperature water. This results in the greater number of $\text{Mg}(\text{OH})_2$ and thinner remaining thickness of MgO film when the film is exposed to the high temperature water.

4 Conclusion

This study demonstrates the influence of water temperature on the dissolution behavior of the MgO (001) thin film and the formation of the $\text{Mg}(\text{OH})_2$ on their surface. Qualitative analysis is done by SEM. The micrographs from SEM show the development of new layers on the film surfaces after being exposed to the water. Meanwhile, XPS depth profile results are in agreement with FIB-SEM cross-sectional results which point out that the MgO thin films are dissolved in deionized water while the dissolution of the films strongly depends on the water temperature. Furthermore, the quantitative analysis is conducted by XPS which indicates the bonding between metallic Mg and hydroxide $-\text{OH}$ in the deconvoluted $\text{O}1s$ spectra. The XPS spectra reflect the amount of the $\text{Mg}(\text{OH})_2$ concentration on the film surface. This result elucidates that after being exposed to the deionized water, the films absorb deionized water and form $\text{Mg}(\text{OH})_2$. This effect is more pronounced in case of the higher temperature. In addition, the information obtained

from this investigation provide the basic understanding of surface science as well as valuable knowledge for the further development and modification which might be a suitable ideal for the industrial processing especially the spintronic device manufacturing. For the next experiment, the dissolution behavior of the MgO thin film under different gas atmospheres will be studied to more recognize the reaction between the MgO thin film and water.

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