



Effect of gas atmospheres on degradation of MgO thin film magnetic tunneling junctions by deionized water

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ABSTRACT

The degradation of the MgO thin film barrier of magnetic tunneling junctions caused by the dissolution of the film in deionized water during manufacturing processes is critical to the performance of spintronic devices. In this work, the influence of gas atmospheres including oxygen (O₂), nitrogen (N₂) and carbon dioxide (CO₂) on dissolution behavior of the film was investigated by using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic absorption spectroscopy (AAS). XPS depth profile results reveal that deionized water reacts with the film and infiltrates into the deeper layer of the film resulting in the chemical transformation of MgO to Mg(OH)₂. AAS results confirm that the films dissolve because Mg²⁺ ions are released into deionized water. Consequently, Mg concentration in deionized water increases. It is found that the concentration of Mg²⁺ ions in deionized water is highest in the dissolution of CO₂-saturated deionized water and lowest in those of N₂-saturated deionized water. Simultaneously, the release of Mg²⁺ causes the development of the coral-like clusters over their surface and a decrease of the film thickness. XPS depth profile and SEM cross-sectional results demonstrate that the film thickness slightly decreases in sample N₂ and decreases considerably in sample CO₂. This is due to the fact that CO₂ gas reacts with water, reducing its pH and thus increasing of the dissolution rate, while N₂ gas has no reaction with water. Finally, this work proposes a qualitative model based on chemical reaction to explain the dissolution behavior of the film.

1. Introduction

Several outstanding properties of magnesium oxide (MgO), including wide bandgap, low dielectric constant, high electrical resistance and high thermal stability [1–3], make it a prominent candidate for various applications including catalysis [4–5], substrate for growing the thin film [6], protective layer for corrosion protection of metals and alloys [7–8] and many other applications. In a past few years, MgO (001) thin film has received a great deal of attention to be used as a tunneling barrier in magnetic tunneling junctions (MTJs) which is a crucial part of read head sensors of hard disk drives (HDDs) [9–10] and magnetic random access memory (See Fig. 1) [11–14]. A primary reason is that MgO thin film barrier is effective in enhancing the tunnel magnetoresistance (TMR) value of MTJs which is correlating with the sensitivity of the read head sensor [15–16]. Theoretically, the maximum TMR value of the MgO-based MTJs was predicted to be 34,000% [17].

Nevertheless, the highest experimental TMR value at room temperature was achieved at 604% [17–19]. To achieve the theoretically predicted TMR value, many studies suggested that controlling the qualities, crystalline orientation, uniformity, and thickness of the MgO thin film are the essential [20–25] because these parameters could be the key factors that affect the TMR value.

The environment of fabrication including temperature and moisture has to be controlled in the manufacturing processes. It is known that the MgO is hygroscopic in nature [26–27]. In the presence of moisture and/or water vapor, MgO naturally absorbs water molecules and, accordingly, forms Mg(OH)₂ layer on its surface [26, 28–29]. These formations of Mg(OH)₂ layer possibly lead to the porosity, cracking and swelling in MgO due to the volume expansion during the conversion of cubic MgO to hexagonal Mg(OH)₂ [29–31]. Nagamine et al. [32] and Singh et al. [27] reported that the residual water that produced in the growth chamber during the thin film deposition process could induce the

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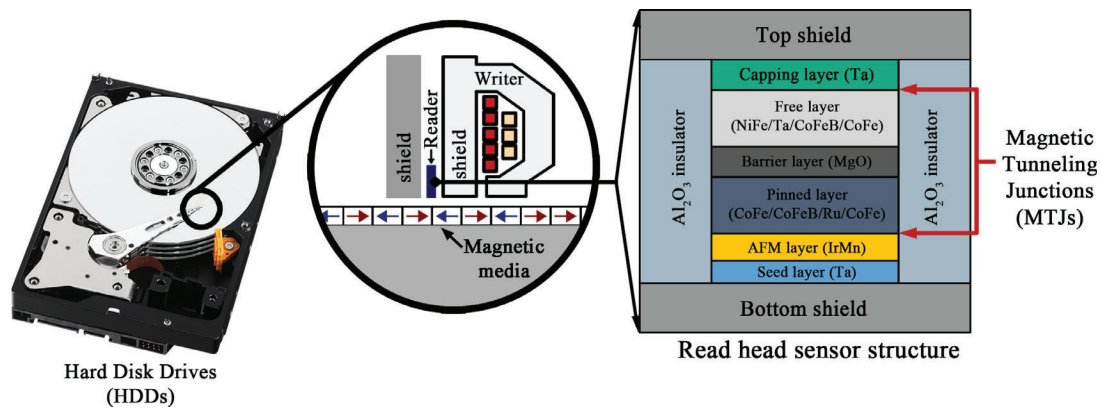


Fig. 1. The read head sensor structure of a hard disk drive (HDD) (Adapted from Ref. [47–48]).

formation of $\text{Mg}(\text{OH})_2$ which resulted in the deformation of the crystalline orientation of MgO thin film barrier. Many studies point out that under dry atmospheric condition, the thin protective MgO film could prevent the corrosion occurred in Mg metals and alloys, however, if it was exposed to aqueous solution, it could promote the formation of high porosity $\text{Mg}(\text{OH})_2$ layer over the MgO film grown on the Mg alloy resulting in the corrosion of Mg alloy [31, 33–36]. From our previous studies [37], we observed that the hydration reaction does not damage only the surface of the film, but it also took place in the deeper layer of the film. This corresponds to the works which done by Lee et al. [28] and Smithson et al. [38]. In the study of Lee et al. [28], it is confirmed that the hydrated MgO could be detected at the inner layer of the film. In addition, Smithson et al. [38] found that the hydration reaction also occurs at the inner part of the MgO particle shell. Besides the hydration reaction, several works point out that if there are significant amounts of water vapor presented and/or MgO is in contact with water, the hydrated MgO can dissolve in water by releasing Mg^{2+} and OH^- ions into water [29, 39–42]. Then, it could lead to an increase in the number of vacancies in MgO [43] and a decrease of MgO thin film thickness [37].

It is clearly seen that the reaction with water does not affect only the properties of the MgO , but it can also change chemical compositions, create vacancies and cracks, decrease the thickness of MgO . Moreover, it is possible that these reactions could reduce the TMR value and hence a decrease in device performance. In magnetic sensor manufacturers, water and/or aqueous solutions are usually applied in cleaning and wet polishing processes [44]. Therefore, it is important to have a better understanding of the reaction mechanism between MgO and water in order to control the quality of MgO thin film. According to the literatures, the factors that can influence the reaction between the MgO and water are the crystallographic orientation of MgO , exposure time, pH, temperature and atmospheres [26, 45–46]. Thus, it is necessary to investigate the reaction between MgO thin film and water under those parameters to obtain information that could be useful for the applications of MgO . From our knowledge, a lot of studies were performed under various solutions, pH and the normal ambient conditions;

however, the influence of gas atmospheres on the degradation of MgO thin film in water have never been addressed in detail. Therefore, in this present study, the profound influence of the gas atmospheres including nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) gasses on the dissolution mechanism of MgO film is investigated. In our work, it was found that the reaction between the MgO thin film and CO_2 -saturated deionized water stronger than those O_2 -saturated deionized water and N_2 -saturated deionized water. The information obtained from this study is valuable and profound knowledge that can be employed as a guideline to prevent the damage of MgO layer due to polishing processes for a hard disk drive manufacture.

2. Experimental

2.1. Sample preparation

MgO (001) thin films with 50 nm of thickness deposited on a Si substrate were supplied by Western Digital (Thailand) Co., Ltd.. The sample was cut into $1.5 \times 1.5 \text{ cm}^2$ square shapes using a diamond scribe. The photoresist layer, designed to protect the film surface, was removed using acetone. Then, the completely removed photoresist MgO thin films were mounted on a custom-built fixture cell, as shown in Fig. 2(a). A Viton O-ring was used to control the dissolved area, such that only the top of film surface was exposed to deionized water (DI water). In the meantime, three different gasses, namely nitrogen (N_2), oxygen (O_2), and carbon dioxide (CO_2), were flowed into DI water, which was then cover on the MgO films. The gas flow rate was controlled by using mass flow controllers. The pH of the DI water was recorded at three different stages: 1) prior to before being saturated with gas; 2) subsequent to before being saturated with gas; and 3) finally, after the dissolution process of the MgO films. The MgO films were covered with DI water which saturated by different gasses for either 1 h or 4 h. This study therefore comprises six conditions of MgO thin film denoted as 1h- N_2 , 4h- N_2 , 1h- O_2 , 4h- O_2 , 1h- CO_2 and 4h- CO_2 .

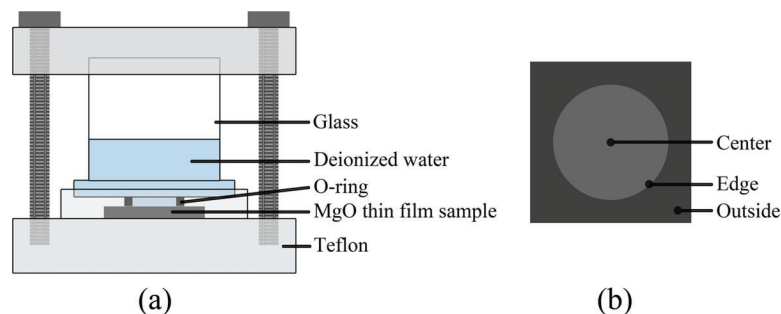


Fig. 2. Schematic diagram of (a) the custom-built fixture cell and (b) the dissolved region of MgO film sample after being exposed to deionized water.

2.2. Characterization

XPS measurements were performed by using a PHI 500 Versaprobe-II located at Beamline 5.3, Synchrotron Light Research Institute (SLRI). An Al $K\alpha$ monochromatic X-ray source (1486.6 eV) in PHI 500 was applied for acquiring XPS spectra. An electron neutralizer was used to compensate for charging effects when studying the insulator surface. For depth profile studies, the MgO thin film samples were etched by 1 kV *in situ* argon ions (Ar^+) with a beam current of 20 mA and $2 \times 2 \text{ mm}^2$ of the beam raster scan. High-resolution spectra of all elements were recorded using 22.4 eV pass energy and a step size of 0.1 eV. Then, for data analysis, the functional composition of each core level was curve-fitted using the CasaXPS software. An in-built Focused Ion Beam and Field-Emission Scanning Electron Microscope (FIB-SEM) was used to determine the surface morphology and the MgO thin film thickness. Three different points of the dissolution regions on the film surface, as demonstrated in Fig. 2(b), were cut cross section by Carl Zeiss AURIGA® CrossBeam® Workstation using a focused Ga^+ ion beam. Cross-sectional images were recorded at a 36° take-off angle using high-resolution SEM. To quantify the concentration of Mg ions which dissolved in DI water, samples of the DI water after the dissolution processes were retained and analyzed using atomic absorption spectroscopy (AAS: Perkin Elmer, PinAAcle900).

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

3.1.1. Thickness of the MgO thin film

The integration of XPS and ions sputtering/etching was used to characterize the depth profile of the MgO thin films. The XPS spectra of the pristine MgO thin film before and after ions etching at 2, 60 and 120 min are presented in Fig. 3. These results reveal that at the beginning, the film is covered by a hydroxide layer and carbon which is likely natural contamination [49]. This contamination was removed by Ar^+ sputtering within 1 to 2 min.

From Fig. 3, if it is assumed that the sample is homogeneous, the quantity of photoelectrons of an element depends on the atomic concentration of that element in the sample [50]. The maximum intensity and the relative sensitivity factor of a peak were used to quantify the relative atomic concentrations of the several constituents of the thin film surface [50]. If the observed elements are detected on the film surface, the concentration of the interested element can be calculated using [49-50]

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x/F_i}{\sum I_i/F_i} \quad (1)$$

where C_x is the atomic concentration of one element in percentage $C_x = \frac{n_x}{\sum n_i} = \frac{I_x/F_i}{\sum I_i/F_i}$ I_x is the maximum intensity of a photoelectric peak of interested element. I_i is the maximum intensity of a photoelectric peak

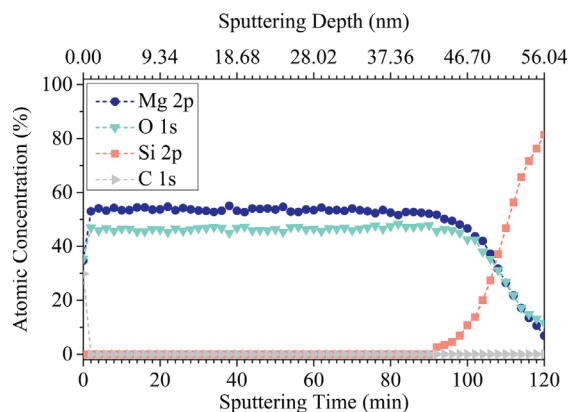


Fig. 4. XPS depth profile of a pristine MgO thin film.

of each element in the sample. F_i is the sensitivity factor of each element in the sample.

By employing Eq. (1), the plot of the atomic concentration of elements as a function of sputtering time of the pristine MgO thin film is presented in Fig. 4. The result reveals that the film consists of the C 1s, Mg 2p and O 1s at the same concentration before the Ar^+ ions etching begins (at 0 min). After the film is bombarded by Ar^+ ions, the C 1s signal decreases to approximately zero whilst the Mg 2p and O 1s concentrations abruptly increase to 50% and then remain stable. After 92 min of sputtering, the Mg 2p and O 1s concentrations slowly decrease to zero while the Si 2p signal, from the silicon substrate, monotonically increases. This expected result is due to the interfacial layer of the MgO/Si and the Si substrate.

Theoretically, the change of the atomic concentration according to the sputtering time is associated with the stoichiometry and the thickness of the films [39]. To convert the sputtering times into the film thickness, the known thickness standard of the MgO thin film is sputtered [49], and the sputtering rate is then calculated using

$$\text{Sputtering rate} = \frac{\text{Thickness}}{\text{Sputtering time (minute)}} \quad (2)$$

In this study, a pristine MgO thin film with 50 nm thickness was used as the standard and sputtering rate of the film is indicated by the point that the Mg 2p line intersects with the Si 2p line (at 107 min). Thus, the sputtering rate of MgO is approximately 0.467 nm/min.

Using Eq. (2), the remaining thickness of each MgO thin film sample is shown in Table 1. A plot of the atomic concentration as a function of sputtering time/depth obtained at the center point of the dissolved regions (See Fig. 2(b)) of the six MgO thin films is presented in Fig. 5. These results demonstrate that the depth profile trend of sample 1h- N_2 and 1h- O_2 is similar to the pristine sample while those of sample 4h- N_2 , 4h- O_2 , 1h- CO_2 and 4h- CO_2 are relatively divergent. These differences are attributed to the different remaining thickness of the MgO thin film.

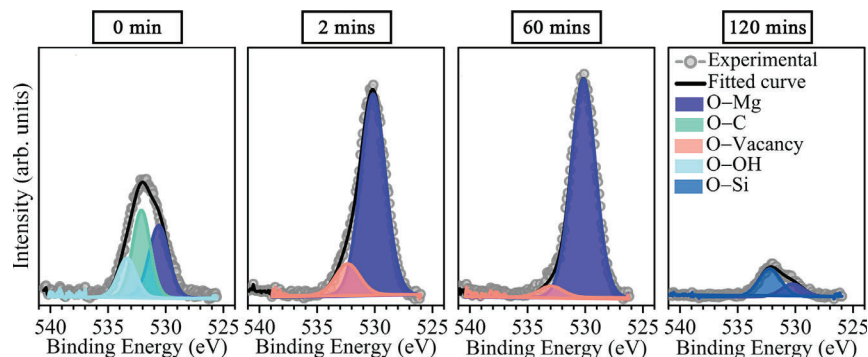


Fig. 3. High-resolution O 1s spectra after 0, 2, 60, and 120 min of sputtering of a pristine MgO thin film.

Table 1

Estimation of MgO thin film remaining thickness using various techniques.

Thickness (nm)	XPS		FIB		AAS	
Conditions	1 h	4 h	1 h	4 h	1 h	4 h
N ₂	40.6	2.8	30	13	$43.7 \pm 0.97 \times 10^{-7}$	$17.5 \pm 3.08 \times 10^{-7}$
O ₂	39.2	0	23	3	$40.7 \pm 2.74 \times 10^{-7}$	$13.5 \pm 2.52 \times 10^{-7}$
CO ₂	0	0	2	0	$22.5 \pm 3.48 \times 10^{-7}$	0

*The error of AAS result obtained from measurement (Fig. 13) and calculation based on mathematical model (Eq. (5)).

The film thickness dramatically decreases in CO₂-saturated DI water and it slightly decreases in N₂-saturated DI water at the same immersion time. It is found that sample 1h-N₂ shows the highest remaining MgO film thickness fraction while the lowest remaining thickness belongs to sample 1h-CO₂, 4h-O₂ and 4h-CO₂. The decrease in film thickness is a result of the dissolution of the MgO thin film in DI water. After the film is covered with gas-saturated DI water, it reacts with water molecules and then dissolves in DI water. It is found that the film reacts strongly with CO₂-saturated DI water, while it only slightly reacts with O₂-saturated DI water and N₂-saturated DI water. This could be attributed to

the pH value of DI water after being saturated by different gasses. Moreover, the result shows that the CO₂ gas significantly dissolves in DI water and reduces the pH of the water while the O₂ gas and N₂ gas dissolves in a small amount in DI water [51]; this will be discussed later in Section 3.4 (effect of deionized water pH).

3.1.2. Formation of mg(oh)₂

To determine the changing of the electronic structure of MgO thin films after being covered with DI water, the high-resolution spectra of all element were deconvoluted and considered. However, only O 1 s

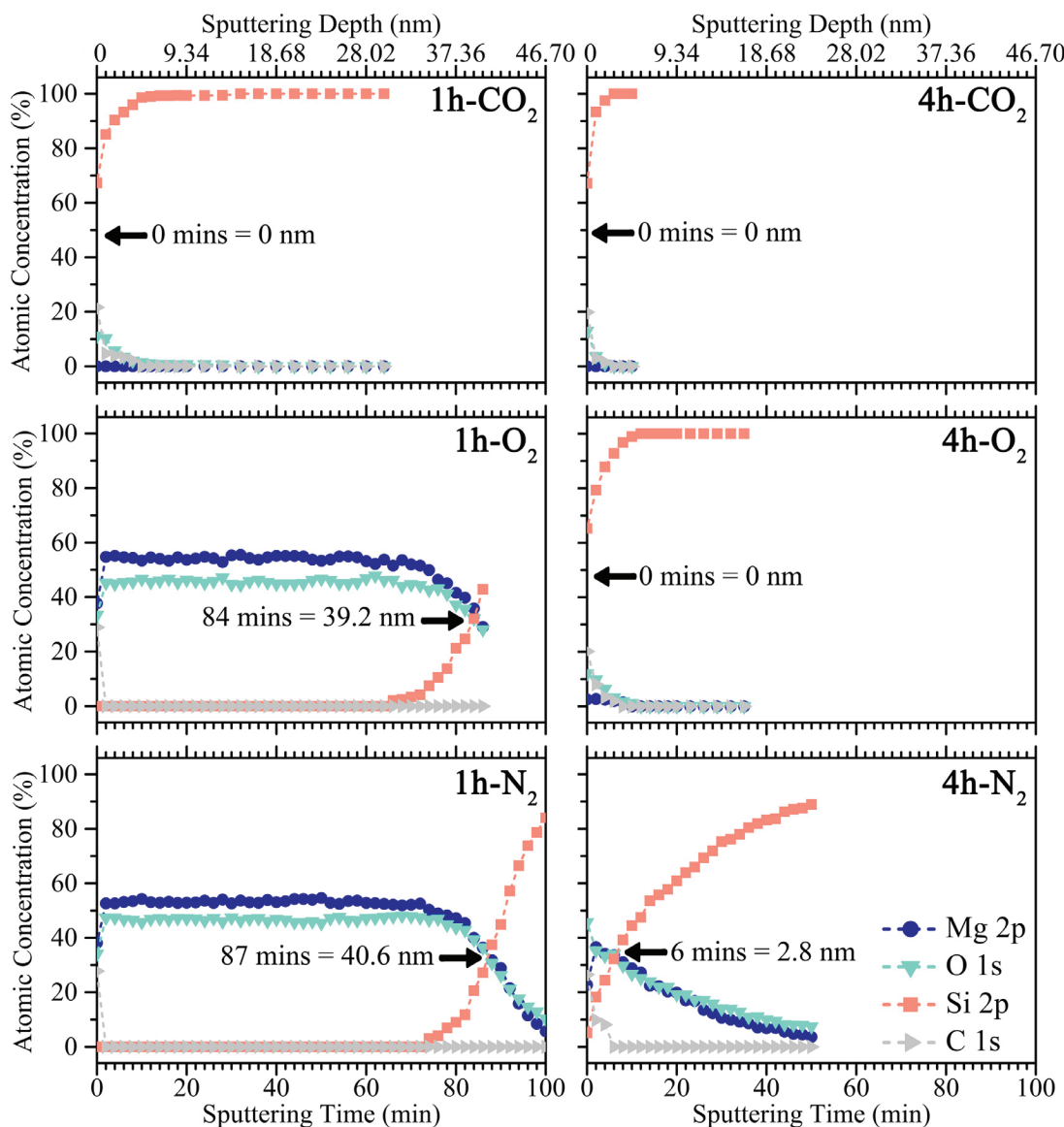


Fig. 5. Depth distribution of MgO thin film atomic concentrations after being dissolved in deionized water under different gas atmospheres. The remaining thickness of the films is indicated by the black arrow.

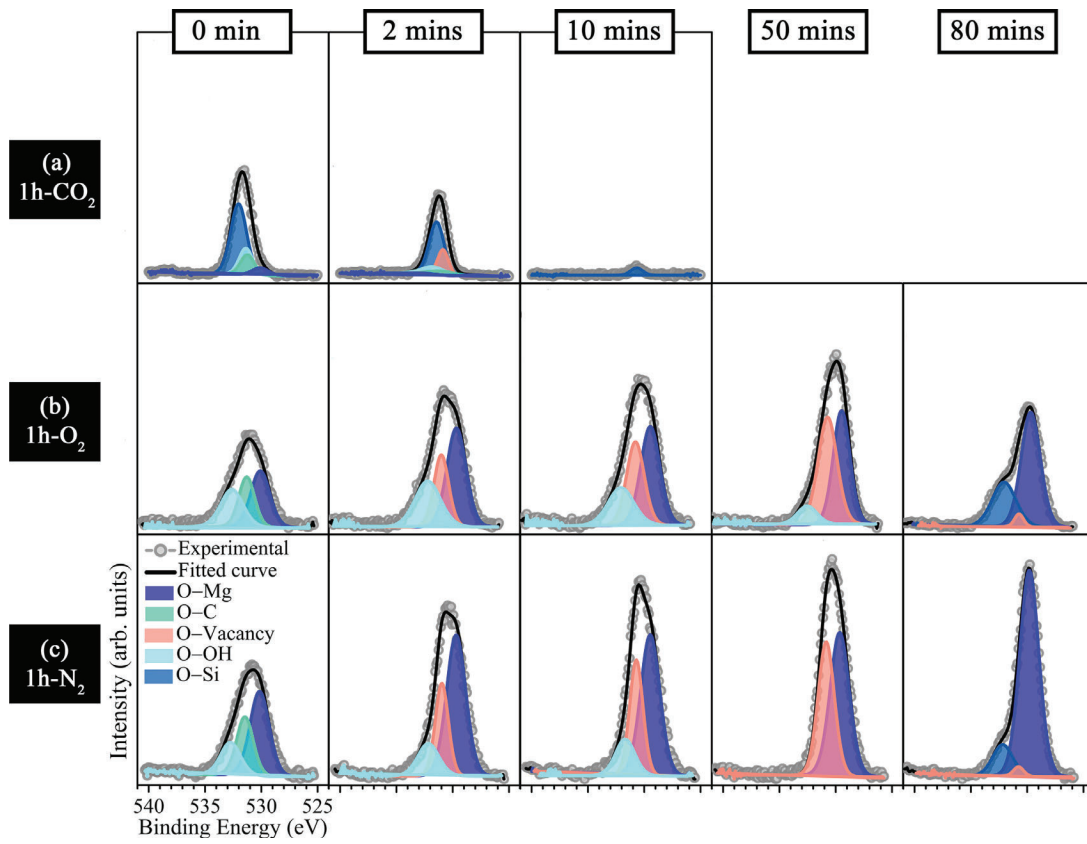


Fig. 6. Variation of high-resolution O 1s spectra which obtained from the MgO thin film after being dissolved in deionized water under different gas atmospheres for 1 h

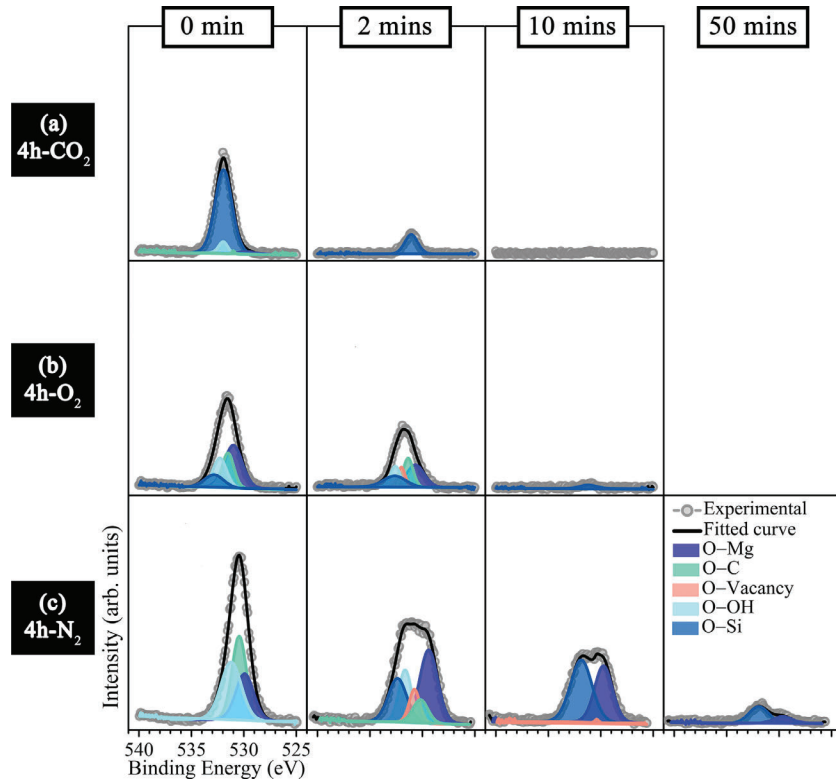


Fig. 7. High-resolution O 1s spectra of MgO thin film after being dissolved in deionized water under different gas atmospheres for 4 h.

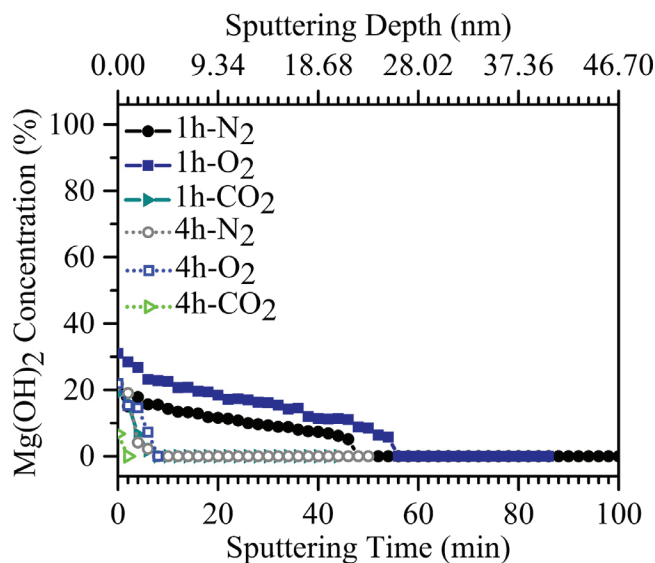


Fig. 8. Atomic concentration of $\text{Mg}(\text{OH})_2$ as a function of sputtering time.

spectra of each sample are represented here. Overall spectra were calibrated by using Ar 2p spectra at binding energy of 243 eV [52–54] to eliminate any positive charge-induced binding energy shift. The secondary electron background of all spectra was subtracted by a Shirley function. A linear combination of 70% Gaussian and 30% Lorentzian peak shape was used to extract the chemical bonding of elements from the respective surface core level [49]. All subpeak of the O 1 s spectra were used Full-width-at-a-half-maximum in a range of 1.5 to 2 eV [55–56]. The characteristics were computed to obtain the best fit of the experiment curve following a least squares minimization method. A significant change of the shape and intensity of O 1 s spectra at selected sputtering times of the six samples are compared in Fig. 6 and Fig. 7.

Fig. 6 presents the high-resolution O 1 s spectra of the samples immersed for 1 h before and after 2, 10, 50 and 80 min of *in situ* Ar^+ sputtering. Before *in situ* Ar^+ ions bombardment begins (at 0 min), the high-resolution O 1 s spectra can be deconvoluted into three subpeaks at 530.1, 531.4 and 532.7 eV for sample 1h- N_2 and 530.0, 531.2 and 532.6 eV for sample 1h- O_2 . On the other hand, the O 1 s spectra of sample 1h- CO_2 can be deconvoluted into four subpeaks at 530.1, 531.2, 532.3 and 533.0 eV. The observed subpeak at binding energy of 533.0 eV of sample 1h- CO_2 is identified as the bonding of O–Si in the SiO_2 lattice (binding energy at 532.8 ± 0.2 eV) [57]. This indicates that the film was wholly dissolved and the silicon from the substrate was detected from the beginning (see Fig. 5). In addition, other subpeaks observed at 530.1 ± 0.2 eV is identified as O–Mg in the lattice of MgO [40, 58–59] and a subpeak at 532.5 ± 0.2 eV is indicated as O–OH in $\text{Mg}(\text{OH})_2$ [59–60]. This implies that the film absorbs the molecules of water and its chemical composition transforms into $\text{Mg}(\text{OH})_2$ [36, 39].

Besides the O–OH and O–Mg subpeaks, observed subpeak at 531.3 ± 0.2 eV are attributed to the bonding of O–C in MgCO_3 from carbon contamination [36, 49, 59, 60]. After 2 min of *in situ* Ar^+ ion sputtering, the O–C subpeaks are completely eliminated from sample 1h- N_2 and 1h- O_2 . It results in the increasing of the O 1 s spectra intensity and shifting of peak position 0.1–0.2 eV toward a lower binding energy. In the meantime, another subpeak at a binding energy of 530.7 ± 0.2 eV is observed in every condition. It is identified as the oxygen-deficient regions within the MgO lattice. These vacancies could be a result of the removal of the oxygen atoms from the MgO lattice during the bombardment of *in situ* Ar^+ ions [58, 61]. After 10 min of sputtering, the intensity of O 1 s spectra of sample 1h- CO_2 considerably decreases to nearly zero while those of sample 1h- N_2 and 1h- O_2 remain as it is. It can be seen that the bonding of O–OH is still detected in

sample 1h- N_2 and 1h- O_2 . This evidence points out that the water molecules do not only absorb on the film surface, but they also infiltrate into the deeper layer of the MgO thin film. These interactions can induce the transformation of the film chemical composition from MgO into $\text{Mg}(\text{OH})_2$. Interestingly, after 50 min of sputtering, the O–OH subpeak disappears from sample 1h- N_2 whilst it is still detected in sample 1h- O_2 . This indicates that the thickness of the $\text{Mg}(\text{OH})_2$ in sample 1h- N_2 is thinner than that of sample 1h- O_2 . This could be because the MgO thin film can absorb the DI water which is saturated by the different gas atmosphere. After 80 min of sputtering time, the O–Si subpeak shows up in both of the MgO samples, indicating that the MgO/Si interlayer is reached.

Next, the immersion time was increased to 4 h, and the change of chemical composition and dissolution behavior was determined again. Fig. 7 presents the deconvolution of the high-resolution O 1 s spectra of the samples before (0 min) and after 2, 10 and 50 min of sputtering. The results show that before the Ar^+ ions etching begins, the O 1 s spectra of sample 4h- N_2 can be extracted into three subpeaks at 529.9, 531.2 and 532.2 eV. Unlike the previous samples, the O 1 s spectra of sample 4h- O_2 and 4h- CO_2 can be deconvoluted into four subpeaks at 530.0, 531.4, 532.4 and 532.8 eV for sample 4h- O_2 and at 530.1, 531.4, 532.3 and 532.9 eV for sample 4h- CO_2 . This is because the signal from the silicon substrate is detected in sample 4h- O_2 and 4h- CO_2 . The coexistence of the O–Mg, the O–OH and the O–Si subpeaks in sample 4h- O_2 and 4h- CO_2 indicates that the hydroxide layer forms at the MgO/Si interlayer region. Furthermore, it could exist in the magnesium silicate phase.

After 2 min of sputtering, the O 1 s spectra of all sample drops. The O–Si subpeak is observed in all samples. At 10 min of sputtering, the O 1 s spectra of sample 4h- O_2 and 4h- CO_2 drastically reduce to zero. It reflects that no oxide/hydroxide film is observed on the silicon substrate. However, the O 1 s spectra of sample 4h- N_2 still remains until 50 min of sputtering. It can be observed that the bonding of O–OH is not detected at 10 min. This can be assumed that the O–OH subpeak is eliminated from sample 4h- N_2 after 4–8 min of sputtering.

To quantify the thickness of the $\text{Mg}(\text{OH})_2$ layer, the integrated peak intensity of O–OH subpeak of high-resolution of O 1 s spectra, as displayed in Fig. 6 and Fig. 7, are converted to the $\text{Mg}(\text{OH})_2$ atomic concentration and then plotted as a function of sputtering time in Fig. 8. The result shows that all samples produce the $\text{Mg}(\text{OH})_2$ over their surface. The $\text{Mg}(\text{OH})_2$ layer generally forms by the transformation of MgO thin film into the hydroxide layer. Thus, the thickness of the $\text{Mg}(\text{OH})_2$ layer is possibly varied according to the remaining thickness of the MgO thin film (See Fig. 5). However, the $\text{Mg}(\text{OH})_2$ is still observed in sample 1h- CO_2 , 4h- O_2 and 4h- CO_2 although the MgO thin film does not exist in these sample. This is because the hydroxide layer form at the MgO/Si interlayer region of these sample. Furthermore, we found that sample 1h- O_2 produces the thicker $\text{Mg}(\text{OH})_2$ layer compared to sample 1h- N_2 . It is because the N_2 -saturated DI water could absorb on the film surface slower than those of O_2 -saturated DI water. The profile of $\text{Mg}(\text{OH})_2$ layer and MgO film after being covered with gas-saturated DI water is presented in Fig. 9.

3.2. Scanning electron microscopy

3.2.1. SEM micrograph

The surface microstructures at the edge of the dissolved region (See Fig. 2) of the MgO thin films after being covered with gas-saturated DI water were examined by using SEM; the results are shown in Fig. 10. The micrographs exhibit that after being covered with gas-saturated DI water, new coral-like clusters are formed over the film surface. From the XPS results, as shown in Fig. 6 and 7, the bonding of O–OH is observed after the deconvolution of O1s spectra. Interestingly, the morphology of these clusters in this study is very similar to the morphology of the corrosion products of the Mg alloy that was reported by Yao et al. [36] Maltseva et al. [62] and Taheri et al. [63–64]. In their

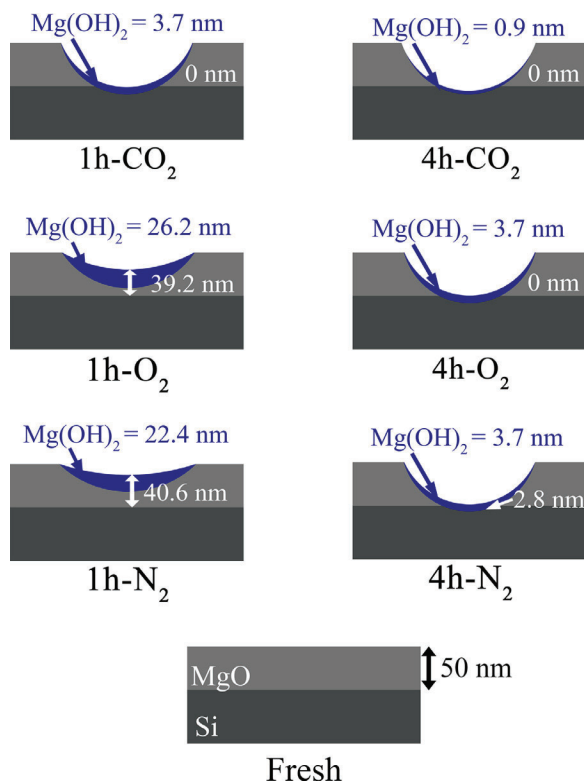


Fig. 9. Schematic representation of the remaining thickness of the MgO thin film and the thickness of the Mg(OH)₂.

work, they found that after Mg alloys were exposed to water, it was corroded by releasing Mg²⁺ ions to water. Then, after the Mg²⁺ ions exceed their solubility limited, it was precipitated as the Mg(OH)₂ at the outmost surface over the top of the MgO film which is formed on the Mg surface [36, 62–66]. The corrosion mechanism is nearly similar to the dissolution mechanism of MgO in this present study which will be discussed later in the section of MgO dissolution mechanism. Therefore, it is possible that these new clusters developed over the sample surfaces could be Mg(OH)₂ layer that formed during the dissolution process.

Significantly, we further found that the development of the clusters strongly depends on the gas and immersion time. The degree of development of the clusters on the surface of sample 1h-O₂ is greater than those of sample 1h-N₂ and 1h-CO₂. Moreover, the number of clusters

also dramatically increase with an increase of immersion time in the case of sample 4h-O₂ and 4h-N₂. On the other hand, there are no new clusters over sample 4h-CO₂ surface. This is because the dissolution rate of the MgO thin film being covered with CO₂-saturated DI water is greater than those of the other gasses resulting in the completely dissolved in CO₂-saturated DI water.

3.2.2. FIB-SEM cross-sectional

Fig. 11 presents the FIB-SEM cross-sectional image at three points of the dissolved region of each sample. The different contrast in the images refers to the different morphology of film and substrate. The darker area corresponds to the substrate region while the brighter area refers to the film region. The remaining thickness of the MgO thin films is evaluated from the cross-sectional images at the three points of the dissolved regions (See Fig. 2(b)) and illustrated in Fig. 12. The thickness of the films at the outside of the dissolved regions remains at ~50 nm, corresponding to the thickness of the pristine sample, as expected since this region of the film is not exposed to water. On the other hand, the film thickness at the other points decreases. We found that the thickness of the MgO thin films at the edge of the dissolved regions remains thicker than those at the center of the dissolved regions. It possibly relates to the capillary action of water which makes the film at the center point absorbs the molecule of water greater than the other points resulting in the higher dissolution rate at that point. The results show that sample 1h-N₂ possess the thickest remaining film while the thinnest remaining film belongs to sample 4h-CO₂. The remaining thickness of the films at the center of the dissolved region are summarized in Table 1.

From FIB-SEM cross-sectional results, we presume the cross-sectional profile of the film after being dissolved as similar to a spherical cap shape. This dissolution profile is used as the model to convert the Mg concentration obtained from the AAS results into the thickness of the film, described next.

3.3. Atomic absorption spectroscopy

Fig. 13 shows the concentration of Mg ions in the DI water, obtained from the different dissolution processes. The results demonstrate that at the same immersion time, the Mg concentration is highest in the dissolution under CO₂ gas and lowest in the dissolution under N₂ gas. This could relate to the reduction of the film thickness as observed in XPS and FIB-SEM cross-sectional results.

The concentration of Mg can be calculated using

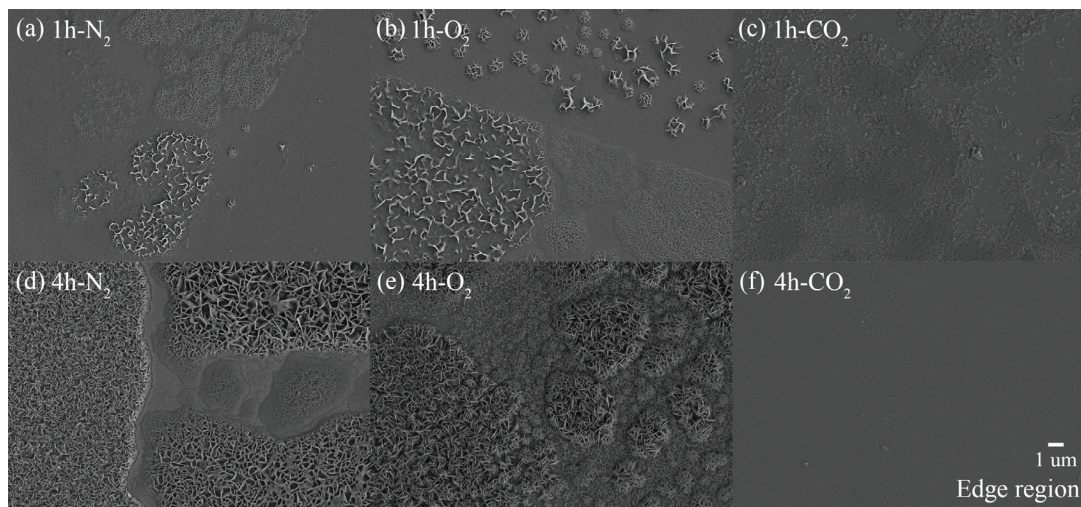


Fig. 10. SEM micrographs (magnification $\times 10,000$) of MgO thin films after being dissolved in deionized water.

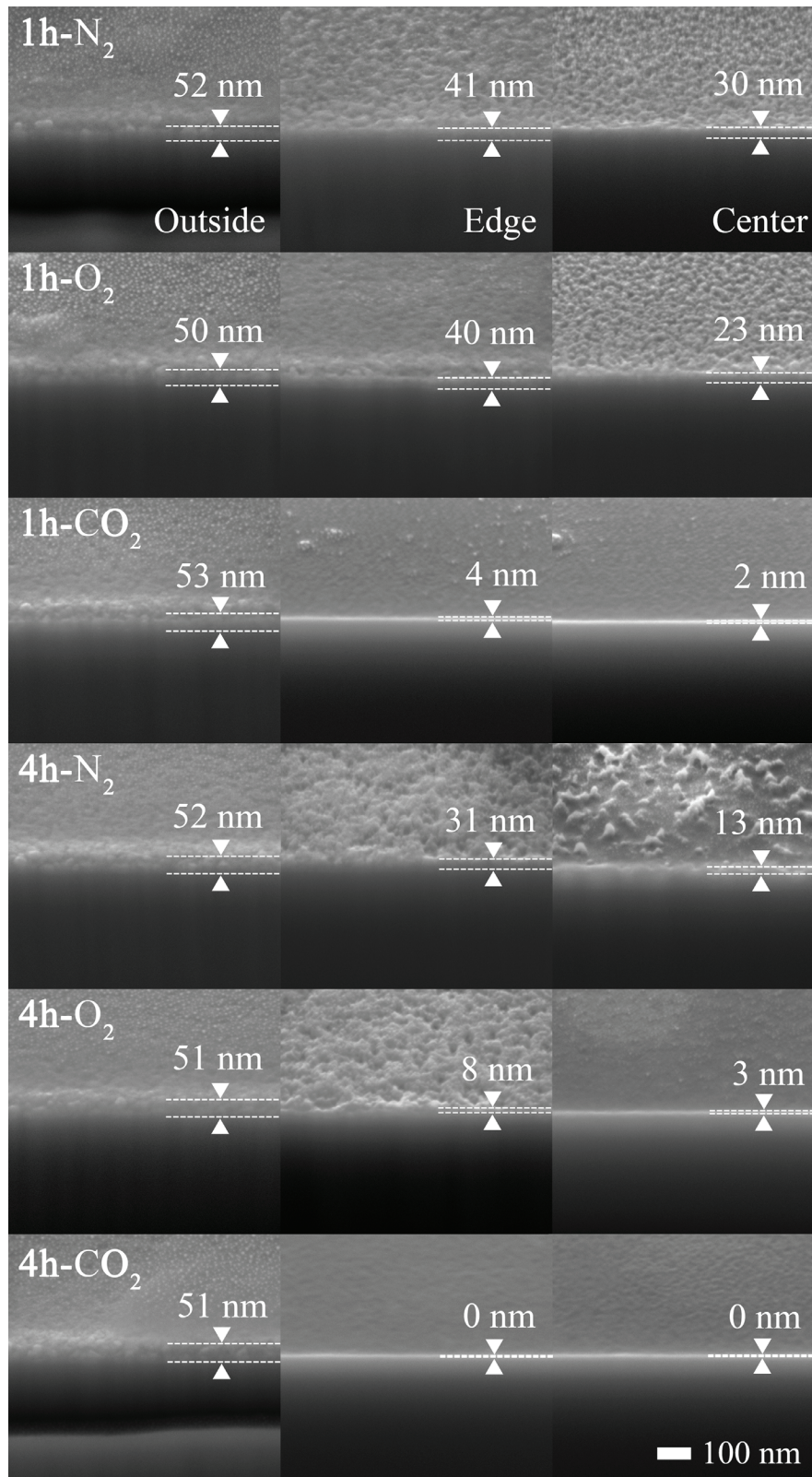


Fig. 11. FIB-SEM cross-sectional micrographs at three points of the dissolved regions of 6 MgO thin film samples (Magnification: $\times 100,000$).

$$C_{\text{MgO}} = \frac{M}{V_{\text{DI}}}, \quad (3)$$

where C_{MgO} is the Mg concentration (mg/L) M is the mass (mg) of the MgO thin film, which is dissolved in the volume, V_{DI} of deionized water (L).

The dissolution profile of the MgO thin films is assumed to be a spherical cap shape. The volume of a spherical cap V_s (nm^3) can be expressed by the formula [67]

$$V_s = \frac{\pi h}{6}(3a^2 + h^2) \quad (4)$$

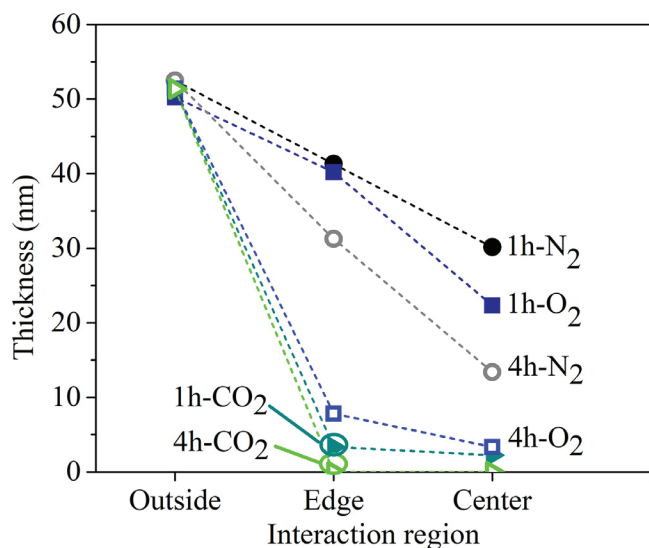


Fig. 12. The remaining thickness of MgO thin films estimated by FIB-SEM.

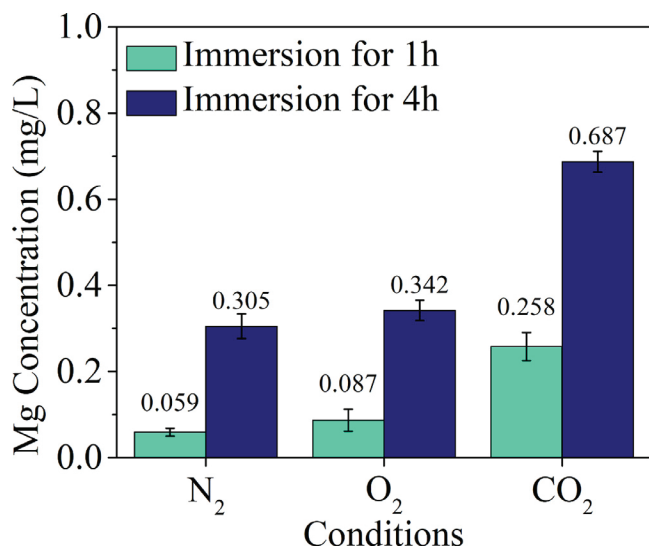


Fig. 13. Mg concentration of MgO thin film which dissolved in deionized water under different gas atmospheres.

where a is a radius of the cap circle or the dissolved region (nm). The mass of MgO thin film (in mg) can be given as $M = DV_s$ while D is the density of the MgO (3580×10^{-21} mg/nm³). Hence, the height of the spherical cap or the thickness of the dissolved film (nm), h can be calculated by combining Eqs. (3) and (4) and expressed as

$$\pi D h^3 + 3a^2 \pi D h - 6C_{MgO} V_{DI} = 0 \quad (5)$$

Therefore, if the thickness of pristine MgO thin film, $T_{standard}$ is 50 nm, the remaining thickness of the films (T_{Remain}) can be estimated by

$$T_{Remain} = T_{standard} - h \quad (6)$$

The remaining thickness of the MgO thin film estimated from AAS results using the Eq. (6) are displayed in Table 1. The trend of the change of remaining thickness obtained from AAS is in agreement with that from the FIB-SEM cross-sectional and XPS.

3.4. Effect of deionized water pH

Fig. 14 presents a plot of the pH values of DI water obtained from three different intervals: 1) before being saturated with gas, 2) after

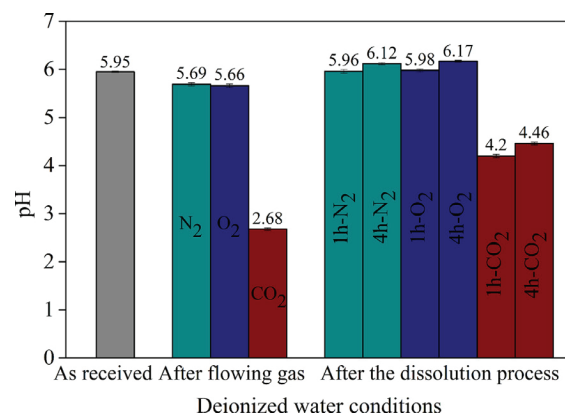
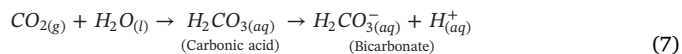


Fig. 14. A plot of the pH values of deionized water obtained before flowing gas after flowing gas, and after the dissolution process.

being saturated with gas and 3) finally, after the dissolution process of the MgO films. The pH of DI water before being saturated with gas is 5.95. After being saturated with gas, the pH of the DI water changed. Interestingly, the pH values slightly decrease in the case of the N₂ gas and the O₂ gas. Unlike the previous cases, pH of the CO₂-saturated DI water dramatically decreases to 2.68. These changes could be attributed to the reaction between DI water and each gas. The International Union of Pure and Applied Chemistry (IUPAC) reported that the solubility of CO₂ gas is 6.15×10^{-4} where as O₂ and N₂ gas are 2.293×10^{-5} and 1.183×10^{-5} , respectively [51]. This confirms that the CO₂ gas dissolves in water higher than N₂ gas and O₂ gas. Generally, the pH of water is determined by the balance of the H⁺ and OH⁻ ions dissolved in water, the higher number of H⁺ ions, the lower the pH [68-70]. It is possible that the gas interacts with the H₂O molecule and then induces the deprotonation of the hydrogen atoms from the water molecule causing the reduction of pH value of DI water. The chemical interaction between CO₂ gas and the water is shown as Eq. (7) [31, 64, 71].



It is found that the CO₂ gas interacts with DI water and produces carbonic acid/bicarbonic acid.

After that, the DI water from the dissolution process was collected. It is found that the pH of DI water tends to increase in every condition while the most significant change of pH is observed in sample 4h-CO₂. Bharadwaj et al. [72] suggested that the higher H⁺ ion concentration in low pH DI water can lead to a higher dissolution rate of the MgO. In addition, Simpson et al. [73] reported that when MgO is exposed to acid, the acidic media adsorbs on the MgO surface leading to surface reconstruction through production of the Mg(OH)₂ layer. Then, Mg²⁺ ions and OH⁻ ions are liberated from the Mg(OH)₂ film and dissolve into the acid solution. These OH⁻ ions dissolved in DI water could result in the increasing of DI water pH as we observed in the DI water obtained from the dissolution process.

3.5. MgO dissolution mechanism

To gain the more understanding of the dissolution behavior of the MgO thin film, the possible reaction mechanism of MgO thin film during being exposed to DI water are concluded from the overall results obtained from several techniques and exhibited as a schematic drawing in Fig. 15. After the MgO thin film is covered with DI water, the film rapidly absorbs the molecules of water on their surface and transforms their chemical composition into Mg(OH)₂ as described by [31, 41]



It is further found that the water molecules continuously infiltrate into the deeper layer of the film resulting in the transformation of the

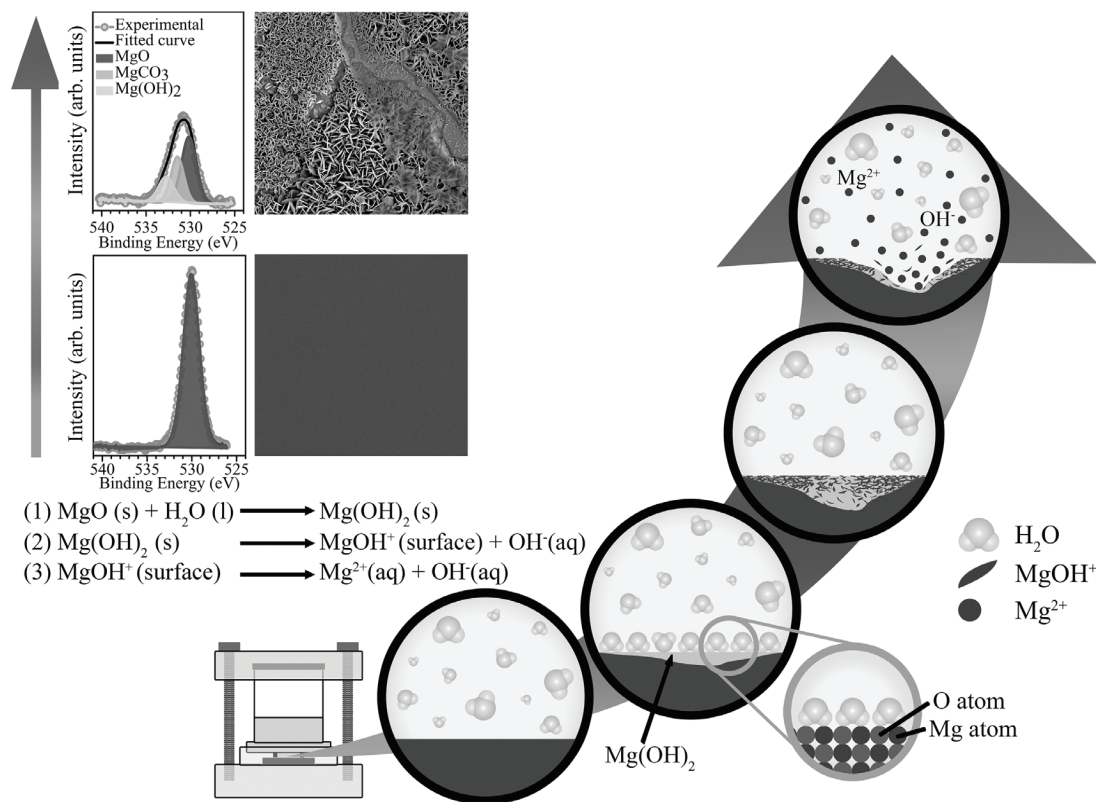
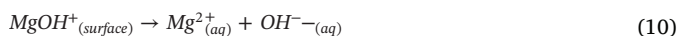
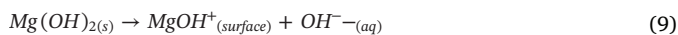


Fig. 15. Schematic diagram of the dissolution mechanism model of the MgO thin film during being exposed to deionized water.

film chemical composition in the deep into Mg(OH)₂ as observed in XPS depth profile results (Fig. 6 and 7). The Mg(OH)₂ layer formed on the film surface starts dissolving in DI water by releasing the OH⁻ ions into the water. Then, the MgOH⁺ layer is reconstructed over the film surface (Eq. (9)) [29, 41–42], which is clearly observed in the SEM images (Fig. 10). The hydroxide layer continuously releases Mg²⁺ and OH⁻ into the DI water, as displayed in Eq. (10) [29, 41–42], resulting in a decrease of the film thickness.



4. Conclusions

This work presents the profound dissolution mechanism of MgO thin films in DI water under the influence of gas atmospheres (N₂, O₂ and CO₂). The results demonstrate that the MgO thin films react with the DI water by the absorption of the water molecules into their surface. The reaction mechanism is nearly similar to the corrosion mechanism of the Mg metal and alloy in water or aqueous solution. Water molecules infiltrate into the deeper layer of the film causing the transforming of film chemical composition into Mg(OH)₂, as observed in XPS depth profile results. It is found that the Mg(OH)₂ layer is thickest in sample 1h-O₂. Furthermore, AAS results reveal that the film dissolves by releasing Mg²⁺ and OH⁻ ions into the DI water. These dissolutions modify the film surface morphology and cause a decrease in the film thickness. It was observed that the film thickness dramatically decreases for dissolution under CO₂ gas, while it only slightly decreases under O₂ gas and N₂ gasses. We found that the dissolution reaction strongly depends on gas atmospheres and immersion times, since the different gas atmospheres affect the DI water pH differently. The CO₂ gas can interact with the molecules of water resulting in the reduction of the pH value of DI water, while on the other hand, N₂ gas has no reaction with the DI

water. These results provide detailed understanding of the influence of various gas atmospheres on the degradation of MgO thin films, and therefore offer important guidelines for quality control and improvement of MTJs sensor manufacturing processes.

CRediT authorship contribution statement

Siriporn Tigunta: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Daniel Sando:** Writing - review & editing. **Narong Chanlek:** Resources. **Laddawan Supadee:** Conceptualization, Resources. **Soodkhet Pojprapai:** Conceptualization, Methodology, Resources, Data curation, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.tsf.2020.138185.

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