



**HAL**  
open science

## Soft X-ray characterization of ion beam sputtered magnesium oxide (MgO) thin film

Mangalika Sinha, Mukul Gupta, Philippe Jonnard, Mohammed H Modi

### ► To cite this version:

Mangalika Sinha, Mukul Gupta, Philippe Jonnard, Mohammed H Modi. Soft X-ray characterization of ion beam sputtered magnesium oxide (MgO) thin film. *Surface and Interface Analysis*, 2018, 50 (11), pp.1145-1148. 10.1002/sia.6446 . hal-01994545

**HAL Id: hal-01994545**

**<https://hal.sorbonne-universite.fr/hal-01994545>**

Submitted on 28 Jan 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Soft X-ray characterization of ion beam sputtered magnesium oxide (MgO) thin film

Mangalika Sinha<sup>1,2</sup>  | Mukul Gupta<sup>3</sup> | Philippe Jonnard<sup>4</sup> | Mohammed H. Modi<sup>1,2</sup>

<sup>1</sup>Soft X-ray Applications Lab, Raja Ramanna Centre for Advanced Technology, Indore 452013, India

<sup>2</sup>Homi Bhabha National Institute, Bhabha Atomic Research Centre, Anushakti Nagar, Mumbai 400094, India

<sup>3</sup>UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452017, India

<sup>4</sup>Sorbonne Universités, UPMC Université Paris 06, CNRS UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, 4 place Jussieu, F-75252, Paris cedex 05, France

## Correspondence

Mangalika Sinha, Soft X-ray Applications Lab, Raja Ramanna Centre for Advanced Technology, Indore 452013, India.  
Email: sinha.mangalika@gmail.com

In the present study, surface and interface characterization of magnesium oxide (MgO) thin film is carried out by using non-destructive soft X-ray reflectivity and absorption technique. To get a further insight about the in-depth and surface composition, secondary ion mass spectroscopy measurement is also carried out. The analysis of the reflectivity data indicates the presence of Mg-Si-O layer between the principal layer (MgO) and Si substrate interface. The secondary ion mass spectroscopy spectra corroborate well with the model assumed in the analysis of the reflectivity data. Combined soft X-ray reflectivity-total electron yield result confirms the presence of low-density MgO on top of principal MgO layer. Total electron yield result confirms the rocksalt structure of the film and provides a glimpse of the electronic structure near the O-K absorption edge.

## 1 | INTRODUCTION

Thin films having nanometre-level thickness has widespread applications in microelectronics, optoelectronic devices, solar cells, semiconductor industry, etc. The advancement of various material growth process using techniques like pulsed laser deposition, ion beam sputtering, and molecular beam epitaxy enables one to fabricate nanometre-level films with high precision. However, the nature of interaction of the deposited film on the substrate is not always known. Sometimes interface formation due to interdiffusion, formation of rough surfaces, and presence of buried layer may hinder the quality of the deposited film resulting in the degradation of its performance in the state-of-the-art optical and electronic devices. Thus, it is a prerequisite to carry out proper material characterization, ie determination of structural parameters with high accuracy, in-depth density profile, surface, and interface composition of the film. Soft X-ray reflectivity (SXR) and soft X-ray absorption spectroscopy (XAS) are powerful techniques used to investigate the surface, interface, and the structural characterization of a thin film. In reflectivity, interference of incident and the reflected X-rays occurs while travelling through different interfaces, which are defined by different distinct refractive indices.<sup>1</sup> Near the absorption edges, with a marginal change in the composition, the atomic scattering factors can vary drastically. Thus, by tuning the photon energy near the absorption edges, one can analyse the in-depth chemical

composition in a non-destructive manner.<sup>2,3</sup> Whereas, in absorption measurements, X-rays are used as a probe to characterize both near-edge features as well as fine structures. X-ray absorption spectroscopy (XAS) measurements are usually performed in total electron yield (TEY) mode. Generally, in TEY mode, the yield current consists of primary Auger as well as secondary electrons. But in the soft X-ray energy range, low-energy secondary electrons consist of a major part of the yield current, making TEY technique much more surface sensitive.<sup>4</sup> Thus, combined SXR-TEY technique is a sensitive probe for surface and interface analysis to determine structural and compositional details.

There are several instances in literature where these techniques are used to successfully describe the interfaces buried deep down the surface. Borrero et al<sup>5</sup> carried out site-selective spectroscopy of transition metal oxide (LaCaMnO<sub>3</sub>/YBCO) heterostructures by using reflectivity and XAS. Filatova and Sokolov<sup>6</sup> have shown the evolution of near edge absorption fine structure of HfO<sub>2</sub> thin film by using simultaneous TEY and X-ray reflection spectroscopy technique. Alders et al<sup>7</sup> also carried out grazing incidence reflectivity and absorption spectroscopy of NiO near Ni 2p edge. In the present work, we have carried out a detailed characterization of surface/interface quality of MgO thin film by using SXR and XAS.

Magnesium oxide (MgO) is well known for its use as a substrate<sup>8</sup> in depositing high-quality oxide films. Thin films of MgO are widely used as a barrier layer in magnetic tunnel junctions.<sup>9-11</sup> Magnesium oxide is also

used as a protective layer in plasma display panel, as well as a buffer layer in high-temperature superconductors. In multilayer mirrors, MgO is used as a spacer layer to get high reflectivity performance in extreme ultraviolet/soft X-ray region.<sup>12</sup> However, to achieve the calculated performance from a thin film/multilayer devices, it is prerequisite to characterize the surface/interface quality in actual energy/wavelength regime. In literature, very few studies on soft X-ray behaviour of MgO thin film are available. In this study, we have carried out SXR measurements of MgO thin film deposited over Si substrate over the wavelength range of 120 to 190 Å. From the analysis of the SXR data, the in-depth delta profile is obtained, which gives a clear picture of density variation near the surface and interface region. The model, as assumed for the analysis of the SXR data, is correlated with the secondary ion mass spectra. The X-ray absorption measurements in TEY mode are carried out near the O-K edge to obtain the information about the top surface layer and the structure of the film.

## 2 | EXPERIMENTAL

### 2.1 | Sample preparation

The MgO thin film of 500 Å thickness was deposited on a Si (100) substrate by using ion beam sputtering technique. Before the deposition, the Si substrate was ultrasonically cleaned. The sputtering of pure MgO target (99.995% purity) was carried out in argon (Ar) environment at a working pressure of  $2 \times 10^{-5}$  mbar. Prior to the deposition, the chamber was evacuated to a base pressure of  $4.2 \times 10^{-7}$  mbar.

### 2.2 | Characterization

Time-of-flight-secondary mass ion spectroscopy (SIMS) measurements were performed by using Cs<sup>+</sup> ion gun operating at 1 keV (TOFSIMS-5, Iontof). However, the analysis was carried by using bismuth (Bi<sup>+</sup>) ions operating at 30 keV, ~4.7 pA. The analysis area was 100 μm × 100 μm inside the sputter crater of 300 μm × 300 μm.

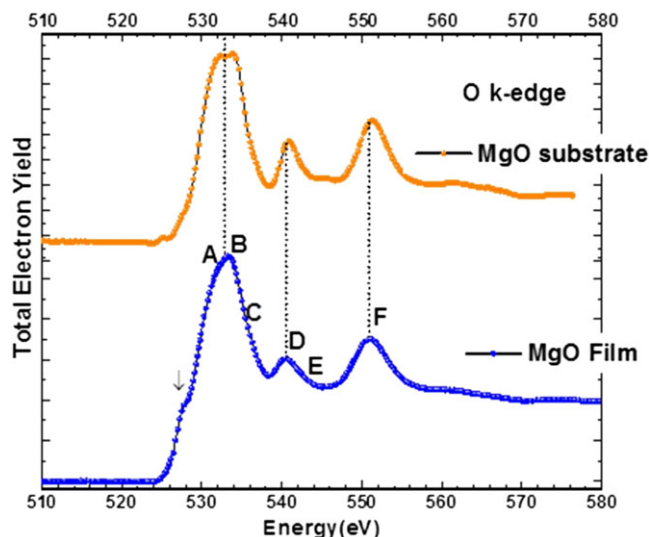
Soft x-ray reflectivity (SXR) measurements were performed in high-vacuum soft X-ray reflectometer installed at reflectivity beamline<sup>13</sup> of Indus-1 synchrotron radiation source. The reflectivity beamline uses a toroidal grating monochromator to provide monochromatic photons in 40 to 1000 Å wavelength range with high flux and moderate spectral resolution ( $\lambda/\Delta\lambda \sim 200$ -450).

The Parratt recursive formalism<sup>14</sup> was used for the analysis of the measured reflectivity data. The surface roughness effect was taken into account by using Névo-Croce model.<sup>15</sup>

Using the XAS beamline at Indus-2 synchrotron source, the O-K edge X-ray absorption spectra (XAS) were recorded in surface sensitive TEY mode.

## 3 | RESULTS AND DISCUSSION

Figure 1 shows the X-ray absorption spectra (XAS) of the MgO thin film near the O-K absorption edge measured in TEY mode. The TEY spectrum shows some fine features that provide information about the structure of the film. In Figure 1, we observe few features that are

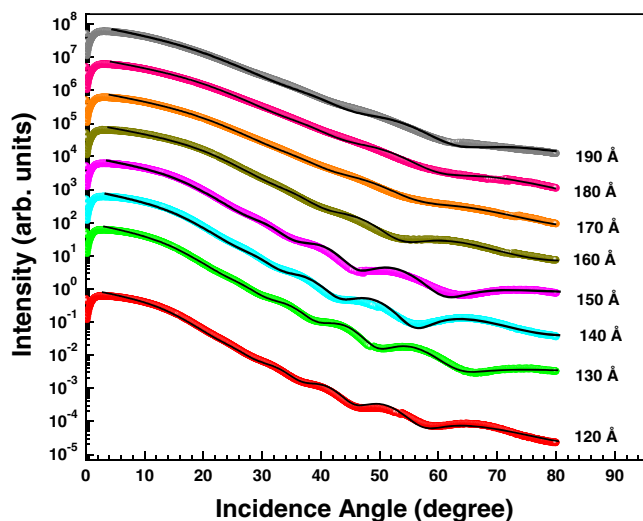


**FIGURE 1** X-ray absorption spectra of 500-Å-thick MgO thin film and that of a MgO substrate measured in total electron yield mode near the O-K absorption edge region

designated as A, B, C, D, E, and F. The features named as A, B, and C arise due to transition from oxygen p → hybridized states of Mg<sub>1</sub> s and Mg<sub>2</sub> s states, where 1 and 2 stands for first and second nearest neighbour Mg atoms respectively. The feature D is due to strong anti-bonding interaction with Mg p orbitals, and the feature E and higher energy features are mainly due to oxygen p → hybridized states of Mg<sub>1</sub> d anti-bonding interactions.<sup>16</sup> One of the features shown by arrow in the spectra could be due to core exciton, which generally expected to appear in the vicinity of the absorption edge. For comparison we have measured the TEY spectra of MgO substrate also. The features appearing in the TEY spectra of MgO substrate is reflected for the MgO film too. In conclusion, the multiple scattering observed in the given spectra can be the direct evidence of the rocksalt structure of the film.

Total electron yield mode is surface sensitive as it provides information about few Å of the surface layer of the thin film. Thus, from XAS measurements in TEY mode, it is confirmed that the surface layer of the film is nothing but MgO only. However, this technique has a limitation to provide information about the interface of the film. To obtain in depth density/composition variation, we have carried out SXR measurements in the wavelength region of 120 to 190 Å.

Figure 2 shows the measured (star) and fitted (black solid line) angle-dependent reflectivity curves of 500-Å-thick MgO thin film using photon beam in the 120 to 190 Å wavelength range. Parratt's recursive formalism was used to analyse the SXR data; the surface roughness was taken into account by using the Névo-Croce model. To obtain a best fit, it is found that a three layer model consisting of the top surface layer, principal MgO layer, and the interfacial layer consisting of native oxide of the substrate is not sufficient to fit the measured data. To improve the fit quality, an additional layer near the film/substrate interface is assumed after the native oxide layer on the substrate. The model that provides a best fit consists of the top surface layer, the principal MgO layer, an interfacial layer consisting of Mg-Si compound, and the native oxide layer on the silicon substrate. The structural parameters, ie thicknesses and roughness of the different layers as obtained from the SXR



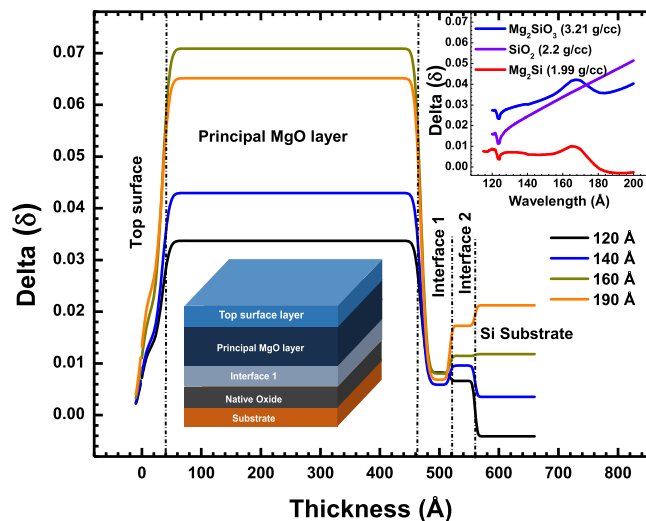
**FIGURE 2** Measured (star) and fitted (continuous solid line) angle-dependent soft X-ray reflectivity curve of magnesium oxide (MgO) thin film over the wavelength range of 120-190 Å

analysis, are tabulated in Table 1. The structural parameters obtained were valid over the complete region of wavelength (120-190 Å) where reflectivity measurements were performed.

The in-depth composition of the MgO thin film can be well understood from the optical density (delta) profile obtained by modelling the reflectivity data and is shown in Figure 3. From the XAS-TEY measurements, it is confirmed that the top layer of thin film is nothing but MgO only, and from the optical density profile (ODP) as obtained from SXR analysis, it is confirmed that the top layer has low density in comparison to the principal MgO layer. Thus, the top surface layer is nothing but low-density MgO layer. From the ODP, it is also evident that the principal layer is almost uniform except near the air/film and the film/substrate interface. The effect of surface roughness is included in the calculation of in-depth ODP as evident from Figure 3, where a gradual change in density (delta) is observed between the interfaces of different layers as assumed in the model. The surface roughness effect is considered in accordance to the Névo-Croce model where an error function instead of a step function is assumed near the interface of different layers. Near the film/substrate interface, formation of some interfacial layer is observed. Previously, Singh et al<sup>17</sup> carried out X-ray reflectivity measurements of Fe/MgO/Fe multilayer stack where MgO buffer layer was deposited on Si substrate to prevent silicide formation at the Si/Fe interface. They observed that the obtained reflectivity pattern matched well with the simulated one on consideration of a SiO<sub>x</sub> and Mg<sub>2</sub>Si<sub>x</sub> layer above the Si substrate. In

**TABLE 1** Structural parameters of the different layers assumed in the analysis of the soft X-ray reflectivity data in the 120-190 Å wavelength range

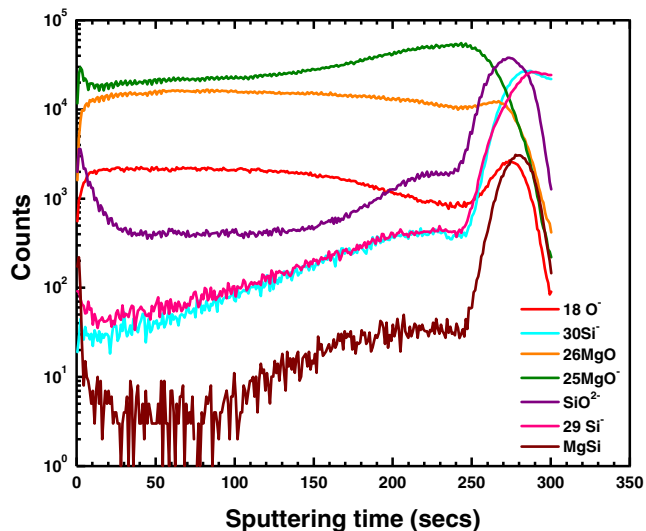
Layer	Thickness, Å	Roughness ( $\sigma$ , Å)
Top surface	35.7	9.3
MgO	434.2	9.2
Mg <sub>2-x</sub> Si <sub>x</sub>	48.2	7.9
SiO <sub>x</sub>	42.6	3.6
Si substrate	INF	3.3



**FIGURE 3** In-depth optical density profile obtained from modelling the soft X-ray reflectivity data. Inset shows the Henke tabulated delta values in the wavelength range of 120-190 Å for bulk Mg<sub>2</sub>SiO<sub>3</sub>, SiO<sub>2</sub>, and Mg<sub>2</sub>Si

our study also, we have considered 2 layers of different densities between the principal MgO and Si substrate. To identify the composition of this interface layer, we tried to make a comparison between the Henke tabulated<sup>18,19</sup> delta values of bulk Mg<sub>2</sub>SiO<sub>3</sub>, Mg<sub>2</sub>Si, and SiO<sub>2</sub>. For 120 Å wavelength, the in-depth delta profile shows that the interfacial layer is actually composed of 2 different layers having a slight contrast in delta, ie having slightly different densities. The two interfacial layers are nothing but Mg-Si-O and Si-O layers. At 120 Å wavelength, the delta value of the first interfacial layer is slightly higher than that of the second one, while at 140 Å wavelength, this trend reverses. This is evident from the inset of the Figure 3, where we can see that the delta value of bulk SiO<sub>2</sub> lies between that of Mg<sub>2</sub>SiO<sub>3</sub> having a bulk density of 3.21 g/cc and Mg<sub>2</sub>Si with a density of 1.99 g/cc. If we consider that the first interfacial layer is composed of Mg-Si-O, then its delta value must lie somewhere between the delta profile of bulk Mg<sub>2</sub>SiO<sub>3</sub> and Mg<sub>2</sub>Si, which is true for our case. Moreover, according to the trend of the delta profile of bulk SiO<sub>2</sub>, it is quite evident that the delta value at 140 Å wavelength for Si-O must be higher as compared with Mg-Si-O. It is also evident from Figure 3 that after 170 Å wavelength, the delta value of the Mg-Si-O layer is quite lower than the Si-O layer. This fact is self-evident if we observe the inset of Figure 3, where we can see that delta value of both bulk Mg<sub>2</sub>SiO<sub>3</sub> and Mg<sub>2</sub>Si follows a decreasing trend as wavelength increases after 170 Å. To confirm the correct picture of the model obtained by analysis of the SXR, we have carried out SIMS measurements. Secondary mass ion spectroscopy being a destructive technique provides the real picture of the in-depth composition of the thin film. Figure 4 shows the SIMS spectra of the MgO thin film, where it is observed that the principal MgO layer is almost uniform throughout the depth of the film except at the film/substrate interface. Near the interface, presence of both SiO<sup>2-</sup> and Mg-Si is evident. It is also evident from the spectra that the Si atoms from the substrate diffused towards the principal MgO layer up to some extent. The Si atoms along with MgO form a complex Mg-Si-O compound. Thus, the SIMS results corroborate well with the ODP obtained by modelling the SXR data.

## ANALYSIS



**FIGURE 4** Secondary ion mass spectroscopy (SIMS) spectra of magnesium oxide (MgO) thin film

## 4 | CONCLUSIONS

Soft X-ray characterization of MgO thin film has been carried out by using SXR and XAS. XAS measurements in surface-sensitive TEY mode near the O-K edge confirms that the top surface of the film is nothing but MgO only. The rock-salt structure of the thin film is also confirmed. Angle-dependent SXR measurements provide information about the structural parameters and the composition at the film/substrate interface. The ODP obtained from SXR analysis confirms the presence of Mg-Si-O and Si-O layers at the film/substrate interface. In-depth profile of the film as obtained from SIMS has also been found to be consistent with in-depth ODP.

## ACKNOWLEDGEMENTS

We are thankful to Mr. Aniruddha Bose for carrying the secondary ion mass spectroscopy (SIMS) measurements. Mr. R. K Gupta and Mr. Udit K. Dewangan are acknowledged for their help during the reflectivity measurements.

## ORCID

Mangalika Sinha  <http://orcid.org/0000-0001-9168-4134>

## REFERENCES

- Zwiebler M, Hamann-Borrero JE, Vafaei M, et al. Electronic depth profiles with atomic layer resolution from resonant soft X-ray reflectivity. *New J Phys.* 2015;17(1-15):083046.
- Sinha M, Modi MH. Depth resolved compositional analysis of aluminium oxide thin film using non-destructive soft X-ray reflectivity technique. *Appl Surf Sci.* 2017;419:311-318.
- Singh SP, Modi MH, Srivastava P. Growth kinetics and compositional analysis of silicon rich a-SiNx:Ha-SiNx:H film: A soft X-ray reflectivity study. *Appl Phys Lett.* 2010;97(1-3):151906.
- Ruosi A, Raisch C, Verna A, et al. Electron sampling depth and saturation effects in perovskite films investigated by soft X-ray absorption spectroscopy. *Phys. Rev B.* 2017;90(1-8):125120.
- Hamann-Borrero JE, Macke S, Gray B, et al. Site selective spectroscopy with depth resolution using resonant x-ray reflectometry. *Sci Rep.* 2017;7(1):13792. <https://doi.org/10.1038/s41598-017-12642-7>
- Filatova E, Sokolov A. Effect of reflection and refraction on NEXAFS spectra measured in TEY mode. *J Synchrotron Radiat.* 2018;25(1): 232-240.
- Alders D, Hibma T, Sawatzky GA, et al. Grazing incidence reflectivity and total electron yield effects in soft X-ray absorption spectroscopy. *J Appl Phys.* 1997;82(6):3120-3124.
- Awaji T, Sakuta K, Sakaguchi Y, Kobayashi T. Improved surface crystallinity of MgO crystal substrate through annealing in oxygen atmosphere. *Jpn J Appl Phys.* 1992;31(5B):L642-L645.
- Yuasa S, Nagahama T, Fukushima A, Suzuki Y, Ando K. Giant room-temperature magnetoresistance in single-crystal Fe/MgO/Fe magnetic tunnel junctions. *Nat Mater.* 2004;3(12):868-871.
- Parkin SS, Kaiser C, Panchula A, et al. Giant tunnelling magnetoresistance at room temperature with MgO (100) tunnel barriers. *Nat Mater.* 2004;3(12):862-867.
- Djayaprawira D D, Tsunekawa K, Nagai M, Maehara H, Yamagata S, Watanabe N, Yuasa S, Suzuki Y, Ando K. 230% room-temperature magnetoresistance in CoFeB / MgO / CoFeB magnetic tunnel junctions. *Appl Phys Lett.* 2005; 86(1), 092502(1-3).
- Pew H K, Allred D D. High throughput reflectivity and resolution X-ray dispersive and reflective structures for the 100 eV to 5000 eV energy range and method of making the devices. US5485499 A.
- Nandedkar RV, Sawhney KJS, Lodha GS, et al. First results on the reflectometry beamline on Indus-1. *Curr Sci.* 2002;82(3):298-304.
- Parratt LG. Surface studies of solids by total reflection of X-rays. *Phys Rev.* 1954;95(2):359-369.
- Nevot L, Croce P. Characterization of surfaces by grazing incidence X-ray reflection. Application to the polishing study of several silicate glasses. *Rev Phys Appl Ther.* 1980;15(3):761-779.
- Luches P, Addato S D' Valeri S, Groppo E, Prestipino C, Lamberti C, Boscherini F. X-ray absorption study at the Mg and O K edges of ultra-thin MgO epilayers on Ag(001). *Phys Rev B;* 69(4): 045412(1-9).
- Singh JP, Gautam S, Singh BB, et al. Magnetic, electronic structure and interface study of Fe/MgO/Fe multilayer. *Adv Mat Lett.* 2014;5(7): 372-377.
- [http://henke.lbl.gov/optical\\_constants/asf.html](http://henke.lbl.gov/optical_constants/asf.html)
- Henke BL, Gullikson EM, Davis JC. X-ray interactions: photoabsorption, scattering, transmission, and reflection at E = 50-30,000 eV, Z = 1-92. *At Data Nucl Data Tables.* 1993;54(2):181-342.