Paper

Investigation of Measurement Conditions of Metastable De-excitation Spectroscopy of MgO Thin Films Used for Plasma Display Panels

K. Yoshino,[1,2,3,*] Y. Morita,[2,3] T. Nagatomi,[1,3,**] M. Terauchi,[2,3] T. Tsujita,[2,3] T. Nakayama,[2] Y. Yamauchi,[4]
M. Nishitani,[3,4] M. Kitagawa,[2] Y. Yamauchi,[5] and Y. Takai[1]

[1]*Department of Material and Life Science, Graduate School of Engineering, Osaka University,*
Suita, Osaka 565-0871, Japan
[2]*3rd Device Development Group, AVC Devices Development Center, AVC Networks Company, Panasonic Corporation,*
Ibaraki, Osaka 567-0026, Japan
[3]*Co-operation Laboratory of Panasonic, Osaka University, Suita, Osaka 565-0871, Japan*
[4]*Advanced Display Technology Group, Image Devices Development Center, Panasonic Corporation,*
Moriguchi, Osaka 570-8501, Japan
[5]*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[*]*yoshino.kyohei@jp.panasonic.com*
[**]*nagatomi@mls.eng.osaka-u.ac.jp*

The measurement conditions of metastable de-excitation spectroscopy (MDS) were investigated in order to apply MDS to the study of the electronic structure of MgO films used for plasma display panels (PDPs). It was demonstrated that positive charging induced on the surface of the MgO film of 50 nm thickness during the MDS measurement can be avoided by employing a low flux of primary metastable He atoms. The positive charges accumulated by successive MDS measurements were found to be completely removed by irradiation of keV electrons, in which the neutralization by the re-distribution of secondary electrons emitted by the keV electron irradiation plays an important role [*J. Surf. Anal.* **12**, 284 (2005)]. The changes in the MDS spectra due to the heating treatment of the MgO film, which is one of the processes employed in the fabrication of PDPs, was investigated, and the ionization potential given as a sum of the band gap and the electron affinity was found to decrease with the increase in the heating temperature. Heating the MgO film at 500°C in vacuum is effective to clean the surface but not sufficient to completely remove contaminations on the surface, and repeating sputtering and heating at 500°C is required to clean the MgO film surface. The electronic structure of the clean surface of the MgO film of 50 nm thickness was found to be the same as that of 500 nm thickness, the thickness of which is a typical value for the MgO film used in PDPs. This result revealed that 50 nm thick MgO films, in which effects of charging is much less than those for 500 nm thick films, can be used to evaluate the electronic structure of the MgO film surface. The present results confirmed that MDS is one of the effective techniques to evaluate properties of MgO films used for PDPs.

1. Introduction

Electron emission phenomena from insulator thin films have been attracting renewed attention because the electron emission property of insulator thin films is one of the most important factors for the further development of alternating-current plasma display panels (AC-PDPs), which has been commercially mass-produced. For further-ing the improvement of PDPs, the reductions in the cost of manufacturing and the power consumption are strongly required, and they can be achieved by reducing the firing voltage of the discharge. The reduction in the firing voltage can be realized by increasing the ion-induced secondary electron (IISE) yield, γ, of a protective layer used in PDP cells [1]. The protective layer is

deposited on the dielectric layer covering electrodes for preventing the surface of the dielectric layer beneath it from being sputtered by plasma, and a commonly used material for protective layers is MgO. Therefore, the measurement of γ has been one of techniques to evaluate the quality of MgO films used for PDPs. However, since a MgO film is an insulator and charged during the measurement of γ, understanding and avoiding charging is essential for the accurate evaluation of MgO films by the γ-measurement. For this end, extensive studies on the IISE from the MgO film surface have been performed [2-13]. The authors have also been involved in the study of the electron emission from insulators under charging [14-19] and from MgO films occurred in PDP panels [20-22].

From a point of view of the interaction between ions having the kinetic energy of below a few keV and the MgO film surface, most of IISEs are considered to be emitted via the Auger neutralization process except for effects of charging on the IISE emission [23,24]. Figure 1 shows the schematic of the IISE emission via the Auger neutralization process. In this process, a primary ion is first neutralized by the transition of a valence electron from the MgO surface to the hole in the ionized shell of the primary ion. Then, another valence electron is excited by receiving a residual energy due to the neutralization. When the energy of the excited secondary electron is higher than the energy barrier at the MgO surface, the secondary electron arriving at the surface escapes from the surface. Therefore, the value of γ strongly depends on the surface electronic states, in particular, the ionization potential, E_{ip}, of the protective layer given as a sum of the band gap energy, E_g, and the electron affinity, χ, i.e., $E_{ip} = E_g + \chi$ [25]. As easily found from the mechanism of the IISE emission via the Auger neutralization process, the protective layer with smaller E_{ip} provides the higher γ. In this regard, E_{ip} is one of the most important factors to evaluate protective layers used for PDPs.

Among several techniques for measuring E_{ip} of solids, metastable de-excitation spectroscopy (MDS) is one of the most powerful approaches for investigating E_{ip} of protective layers. MDS can provide the information on the electronic structure at a few Å above the surface as mentioned in section 2. The IISE emission via the Auger neutralization process is significantly affected by the electronic structure in the outermost surface region since

the neutralization of primary inert gas ions, which are gas species used as the discharge gas in PDPs, occurs in the outermost surface region. In addition, the MDS spectra can provides E_{ip} as well.

In this study, therefore, we applied MDS to the investigation of the electronic structure of the MgO film surface used for PDPs. For this, since the MDS measurement induces the positive charging of the MgO surface, we investigated measurement conditions of MDS to avoid and remove positive charging in order to measure the electronic structure of MgO films with high reproducibility. Changes in the MDS spectra by the heating treatment and the dependence of the MDS spectra on the thickness of the MgO film were also investigated.
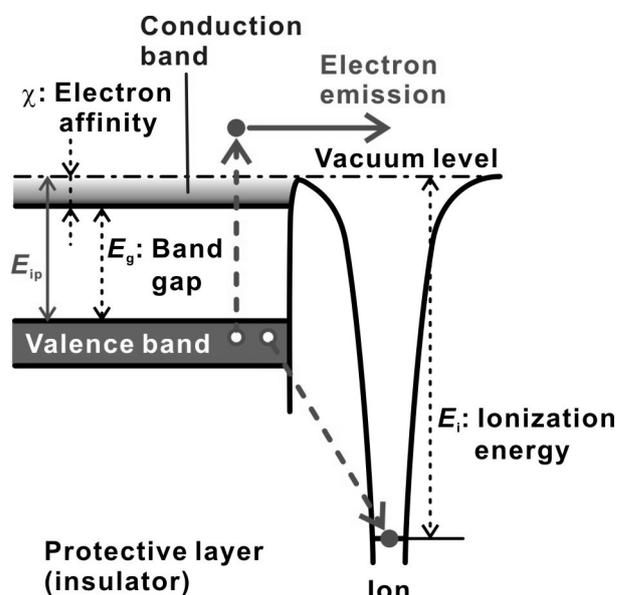

Fig. 1. Ion-induced secondary electron emission from the insulator surface via the Auger neutralization. E_{ip} is the ionization potential of an insulator given as $E_{ip} = \chi + E_g$.

2. Experiments

All measurements of MDS were performed using apparatus developed and operated at National Institute for Materials Science (NIMS). A metastable He atom (He*) source is attached to an analysis chamber, the base pressure of which was 2×10^{-8} Pa. An ion gun for sputter cleaning and a cylindrical mirror analyzer (CMA) with a coaxial-type electron gun (PHI590A) are attached to the analysis chamber. The CMA system enables the measurement of Auger electron spectroscopy (AES) spectra

and electron energy spectra for MDS. The details of the experimental apparatus are described elsewhere [26].

Figure 2 shows the mechanism of the electron emission from insulators in MDS. MDS is a surface analytical technique for investigating the electronic structure just above the sample surface by measuring an energy spectrum of electrons emitted by the impact of He*. When a primary He* approaches to the sample surface, 1s and 2s electrons in He* interact with the solid surface at around 2 to 4 Å above the surface. Since the sample in the present experiments, MgO, is the insulator, no resonant transition of a 2s electron in He* to the sample surface occurs, and the Auger de-excitation process takes place. A valence electron in MgO transits to the hole in the 1s orbit of He*. The residual energy in this transition is transferred to a 2s electron, and, then, the 2s electron is emitted from He*. Since the amount of the residual energy is determined by the difference in the energy of valence electrons in MgO and the binding energy of the 1s electron in He*, the energy distribution of emitted electrons via the Auger de-excitation process ideally represents the density of states (DOS) of MgO just above the surface. In actual measurements, interactions of electrons emitted from He* and the sample surface occurs, and electrons, such as low-energy secondary electrons, are also emitted from the sample surface. Therefore, electrons in the high-kinetic energy region in MDS spectra are dominated by the DOS in the vacuum side of MgO and those in the low-kinetic energy region are dominated by the low-energy secondary electrons emitted from the sample surface.

The sample used in the present study was a MgO film of 50 nm thickness deposited on the n-type Si substrate (1~10 Ωcm). The MgO film was deposited on the substrate by the electron beam deposition in atmosphere of O_2 at 4×10^{-2} Pa with the substrate temperature of 310°C. The sample was cut into the size of ~10×10×0.5 mm^3 and introduced into the MDS measurement chamber without any pretreatment. The sample surface was cleaned by repeating sputtering for 10 min and heating at 500°C for 1 min in the MDS measurement chamber as mentioned in detail in section 3.1. The sputter cleaning was performed using 1 keV Ar$^+$ of ~0.3 μA with the beam diameter of ~2 mm. The ion beam was scanned over the region of 20×20 mm^2. The sample heating was performed by the electron bombardment from a W fila-

ment located behind the sample. The cleanness of the sample surface was confirmed by AES and the cleaning process was continued until no carbon peak was observed in an AES spectrum. The AES measurement was performed using 3 keV electrons of 150 nA with the diameter of 1 μm at the normal incidence without scanning. The typical number of repeating the sputtering and heating to clean the MgO film surface was two.
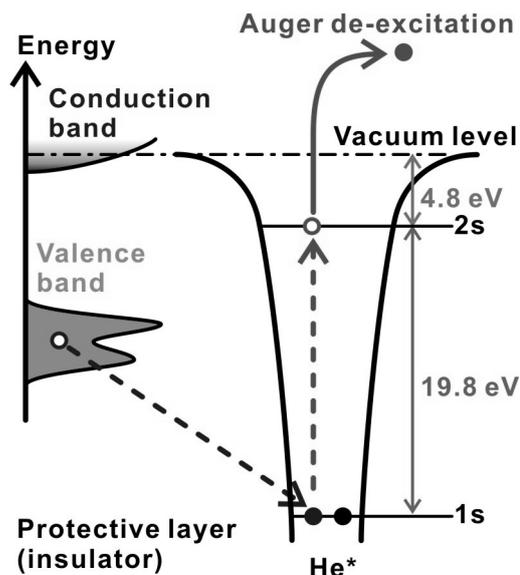

Fig. 2. Schematic of the electron emission from insulators via the Auger de-excitation process in MDS.

The quantitative measurement of the flux of primary He* by means of conventional methods, such as the sample current measurement, is very difficult because the number of electrons emitted from the sample surface is significantly sensitive to conditions of both the sample surface and measurement conditions, such as the incident angle of He*. Therefore, we monitored the flux of primary He* by measuring the sample current when primary He* was irradiated onto the reference Au. The typical value of the sample current resulting from irradiation of He* onto the Au sample was ~10 pA in the present study. The bias voltage applied to the sample during MDS measurements, V_{bias} (<0), was typically around -25 V, which is required to measure the onset of the electron spectrum consisting of low-energy electrons as those done for the measurement of E_{ip}, i.e., the work function for metals, using ultraviolet photoelectron spectroscopy (UPS) [27] and the secondary electron method

[14,28-31].

3. Results and discussion

3.1. Changes in MDS spectra by cleaning of MgO surface

   Figure 3 shows MDS spectra obtained for a MgO film on the Si substrate after heating at different temperatures of 100 to 500°C. Since the heating treatment in vacuum has been used for outgasing the MgO film in the manufacturing process of PDPs and was used as a cleaning process with the combination of sputtering in the present study, effects of heating on an MDS spectrum of the MgO film was investigated. It is found that the MDS spectra hardly change upon heating below 200°C, and the spectrum shape gradually changes above 300°C. The peak intensities located at the higher- and lower-energy sides increase and decrease, respectively, with increasing the temperature. The energy of the peak at the higher-energy side shifts towards the higher-energy by heating at 300°C as confirmed from the dotted lines. At the same time, the tail at the higher-energy side shifts toward the higher energy. Taking into account the fact that decomposition of $Mg(OH)_2$ and $MgCO_3$ and the desorption of their components take place by heating at above 300°C [32,33], it is considered that the change in the MDS spectra of the as-received MgO film by heating at above 300°C is attributed to the change in the surface composition. Note that the AES measurement after the MDS measurement shown in Fig. 3(f) revealed that the sample surface is still contaminated by a small amount of carbon, indicating that the heating treatment carried out for the measurement shown in Fig. 3 is not enough to completely remove the surface contaminations from the MgO film surface.

   For the cleaning of the MgO film surface, sputtering by 1 keV Ar^+ irradiation and heating at 500°C were repeated. Figure 4 shows AES spectra obtained for the as-received and cleaned MgO film surfaces. It is clearly observed that the C-KLL peak originated from surface contaminations disappeared after the cleaning. The MDS spectra obtained for the clean MgO surface is also shown in Fig. 3(g). It is clear that the peak at the higher-energy side in the MDS spectrum shifts toward the higher energy after cleaning. The series of MDS spectra shown in Fig. 3 revealed that the surface electronic structure of the MgO film is strongly affected by the surface contamina-

tion, suggesting that γ, which is sensitive to the electronic structure of the surface, might be also affected by the surface contamination of the MgO film.
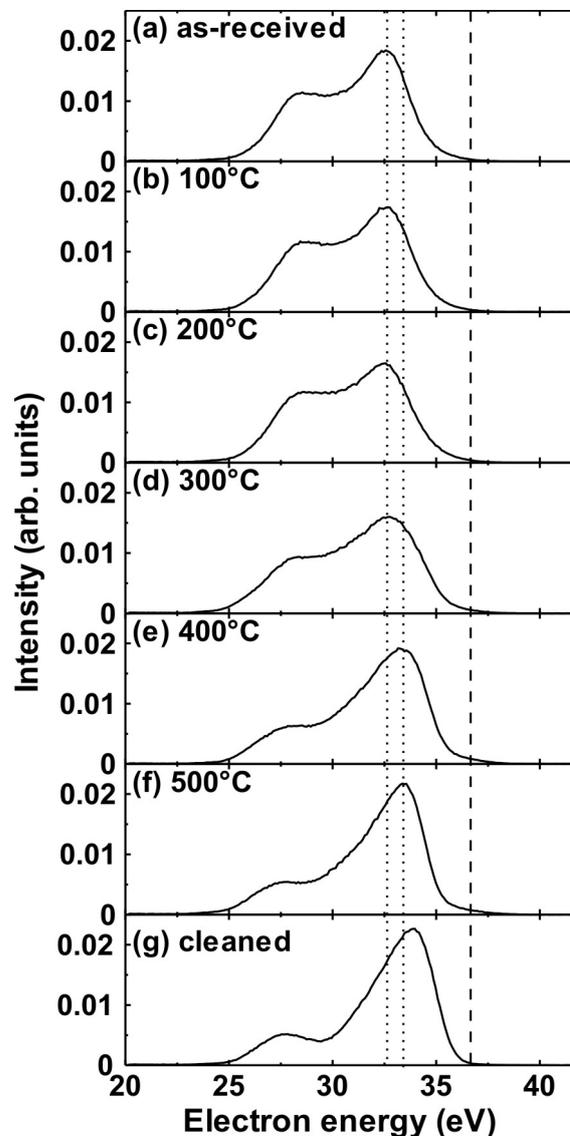

Fig. 3. MDS spectra of the MgO film of 50 nm thickness on the Si substrate obtained (a) for the as-received sample and after heating the sample at (b) 100, (c) 200, (d) 300 (e) 400, and (f) 500°C, respectively, with increasing the temperature with the interval of 100°C. The sample was heated at each temperature for 1 min and the MDS spectra were measured after the sample being cooled. (g) An MDS spectrum obtained for the MgO film of 50 nm thickness after cleaning by repeating sputtering with 1 keV Ar^+ ions and heating at 500°C. The bias voltage applied to the sample during the MDS measurement was -24.6 V. The dotted lines show the peak positions of the MDS spectra shown in Figs. 3(a) and (f). The broken line is a guide to shows the energy of the tail at the high-energy side.
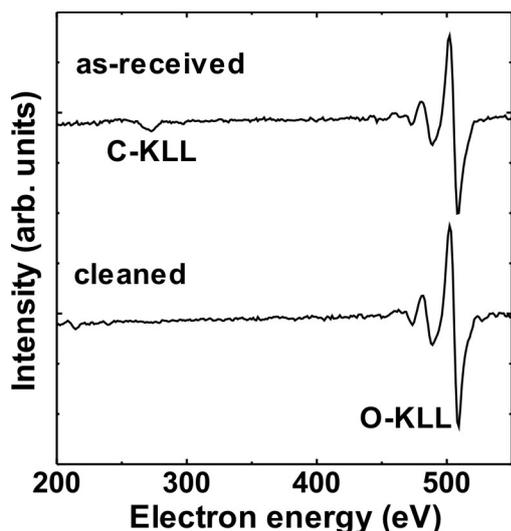
Fig. 4. AES spectra obtained for the as-received and cleaned MgO film surface.

3.2. Charging during MDS measurement and neutralization by high-energy electron irradiation

Figure 5 shows the MDS spectra of the cleaned MgO film surface obtained for different fluxes of primary He[*]. The ratio of the fluxes of primary He[*], which were roughly estimated from the sample current during the MDS measurement, in (a) to (d) were 50:15:3:1. It is clear that the MDS spectra shift towards the lower-energy side with the increase in the spectrum number when the flux of the primary He[*] is high. The intensity of the spectra also decreases with the increase in the spectrum number. The shift in the peak position and the decrease in the intensity are attributed to the positive charging of the MgO film surface induced by the electron emission due to the irradiation of He[*]. In contrast to the case of the high flux of primary He[*], the MDS spectra do not change when the flux of primary He[*] is low as confirmed in (c) and (d). The present results confirmed that MDS spectra of the MgO film of 50 nm thickness can be measured without effects of charging by lowering the flux of primary He[*], and all measurements described below were performed under such a condition, where no charging was induced except for Figs. 5 and 6.

Although the low flux of primary He[*] enables the MDS measurement to be performed without observable charging during successively measuring a few MDS spectra, successive measurements might induce charging, and the neutralization of charging is required. With respect to the positive charging induced on the MgO film

of 50 nm thickness under positive ion irradiation, it has been reported that the irradiation of energetic electrons of a couple of keV can remove positive charging, in which low-energy secondary electrons emitted by the electron irradiation are trapped by the positive surface potential and mediate charging [17]. The electron irradiation itself does not induce charging because of the so-called electron-beam induced conduction since the range of primary electrons exceeds the film thickness [17]. In order to confirm the effectiveness of the irradiation of electrons to removing positive charges on the MgO surface induced by the MDS measurement, 3 keV electrons of 150 nA were irradiated onto the MgO surface. Ten MDS spectra were successively measured in one cycle, and 3 keV electrons are irradiated before the next cycle. Four cycles of the MDS measurements were repeated and the irradiations of 3 keV electrons for 10, 60, and 300 s were performed after the first, second, and third cycles of the MDS measurements. The MDS spectra were measured for four different fluxes of primary He[*] as done for Fig. 5.

Figure 6 shows the results of the investigation of the neutralization of positive charges induced on the MgO film surface during the MDS measurements, where the intensity and energy of the peak at the high-energy side are plotted as a function of the number of spectra. For comparison, the MDS spectra corresponding to those obtained by the first measurement in each cycle are shown in Fig. 7. The decrease in the peak intensity and the shift in the peak position are significant for the higher flux of primary He[*] as expected from Fig. 5. At the lower flux of primary He[*], the decrease in the peak intensity and the shift in the peak position were not observed, indicating that no charging was induced under that experimental condition. Although the changes in the peak position and intensity are significant for the higher flux of primary He[*], it is found that the peak position and intensity are completely recovered by the irradiation of 3 keV electrons. This is also confirmed from Fig. 7, where the first MDS spectra in each cycle are plotted, and all the first MDS spectra in each cycle agree with each other. The time of the electron irradiation for the neutralization was varied from 10 to 300 s and it is revealed that the positive charging of the MgO surface induced by the measurement of 10 MDS spectra is completely removed under all conditions of the electron irradiation. From

these results, we determined that all the MDS spectra for MgO films of 50 nm thickness were measured with the flux of primary He* of around that used for the measurement of Figs. 5(c) and 7(c). This flux is 1/1000 of those used in conventional MDS measurements for conductive samples, i.e., the sample current measured by the reference Au of ~10 pA. In addition, even though the flux of primary He* is sufficiently low to measure ten MDS spectra without charging, the irradiation of 3 keV electrons of 10 s was performed after each MDS measurement in order to avoid the accumulation of the charge during successive MDS measurements. Note that the MDS spectra shown in Fig. 3 were measured with the low flux of primary He* to avoid charging.

3.3. Dependence of MDS spectra on sample bias

The MDS measurement can provide the information on the ionization potential E_{ip}, i.e., the work function for metals, of insulators as that provided by UPS. For such a measurement, we need to measure the width of a spectrum i.e., the onset and cutoff energies of a spectrum. Hereafter, we define the onset and cutoff energies of the spectrum as the minimum and maximum energies of the MDS spectrum. Because there is the difference in the vacuum level between the sample and spectrometer, the sample was negatively biased to detect all of low-energy electrons emitted from the sample surface [14,27-31]. In such a measurement, the linearity of the energy scale should be confirmed when different sample biases are applied. For this, the MDS spectra of the MgO film were measured by applying different sample bias voltages of
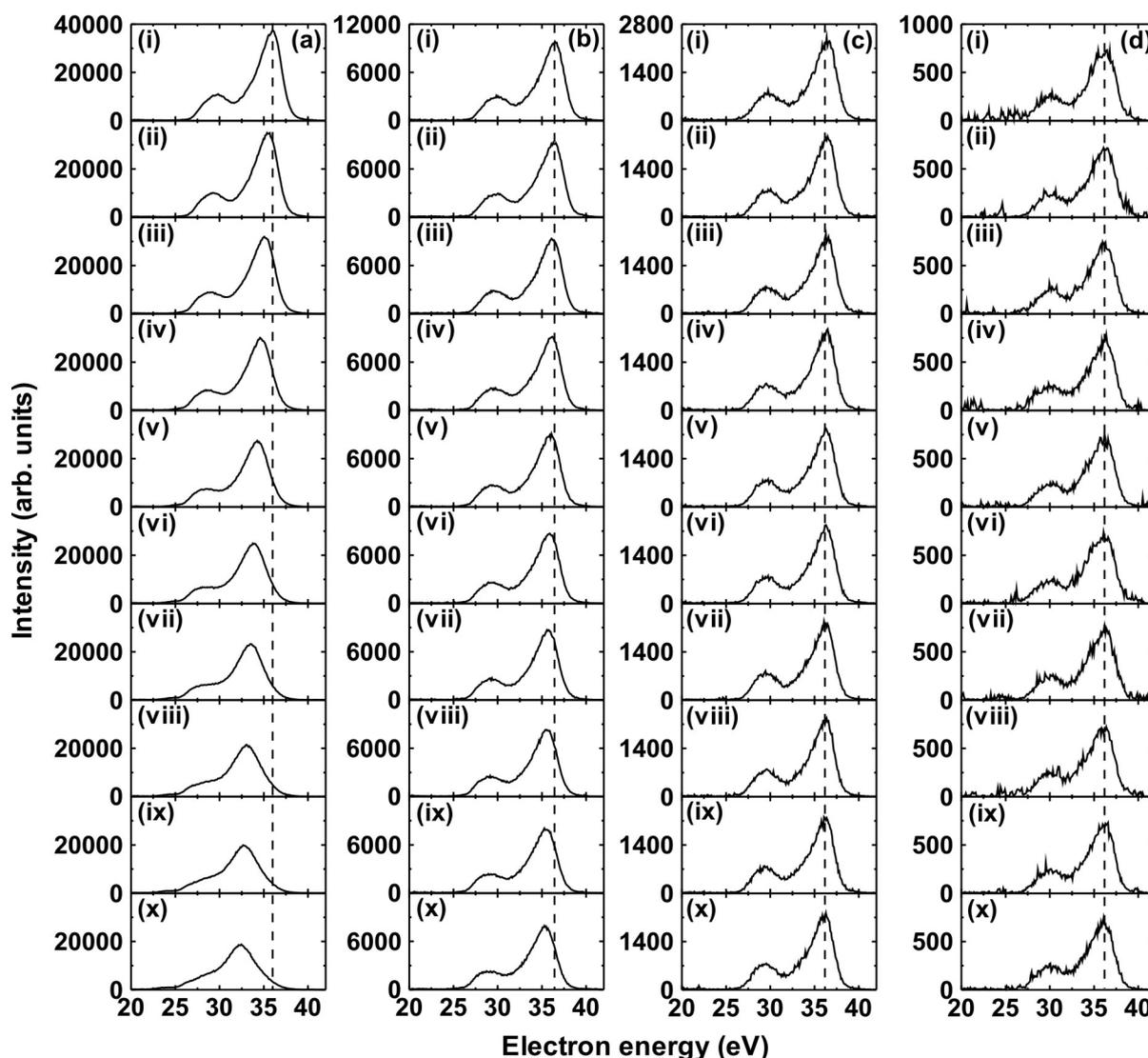

Fig. 5. MDS spectra obtained for different fluxes of primary He*. The ratio of the fluxes of primary He* roughly estimated from the sample currents are (a) 50, (b) 15, (c) 3, and (d) 1. In each panel, spectra (i) to (x) were those successively measured. The first spectrum (i) in each panel was measured immediately after the neutralization of the MgO film surface. The dotted line in each panel represents the peak position of the first MDS spectrum (i). The bias voltage applied to the sample was -25.8 V.

-9.2 to -28.3 V. The resultant MDS spectra are shown in Fig. 8. It is found that the MDS spectra almost linearly shift toward the higher-energy side with the increase in the sample bias voltage. The spectrum shape does not significantly change for different bias voltages.

that the energy scale of the spectrum, i.e., the width of the MDS spectrum, can be corrected by dividing by the correction factor of 0.94 when the energy range of the spectrum is between 22 and 41 eV under the condition of the sample being biased from -9 to -28 V.
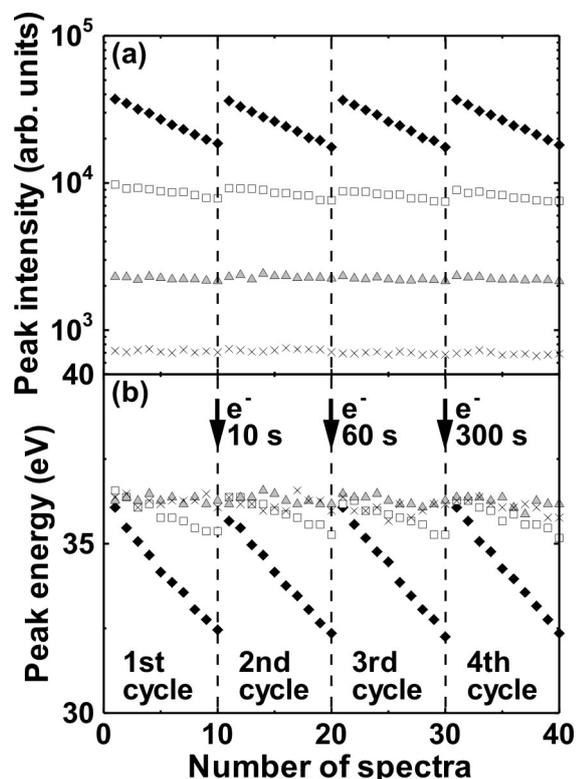

Fig. 6. (a) Intensity and (b) energy of the peak at the high-energy side of MDS spectra from the MgO film of 50 nm thickness. In each cycle of measurements, ten MDS spectra were successively measured. After finishing the measurement in each cycle, 3 keV electrons of 150 nA were irradiated for the neutralization. The irradiation times of electrons were 10, 60, and 300 s at the end of the first, second, and third cycles, respectively. Diamonds, open squares, triangles, and crosses correspond to those obtained from MDS spectra measured at the different ratios of fluxes of primary He* of 50:15:3:1 as those in Fig. 5. The bias voltage applied to the sample during the MDS measurement was -25.8 V.
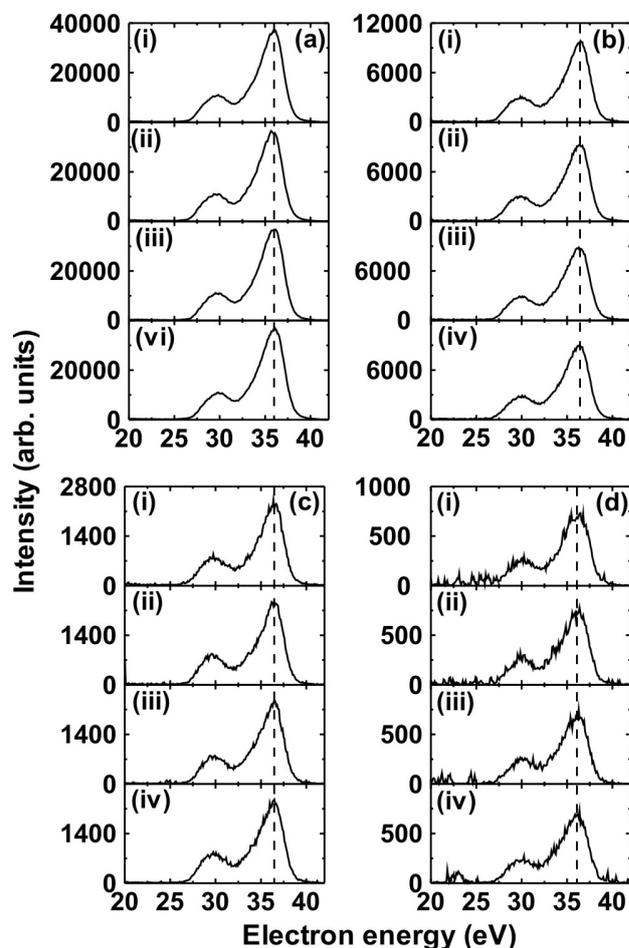

Fig. 7. MDS spectra obtained with the neutralization by the irradiation of 3 keV electrons. The experimental conditions correspond to that for Fig. 6. (a) to (d) show the MDS spectra obtained at the different ratios of fluxes of primary He* of 50:15:3:1, as those for Fig. 6. (i) to (iv) in each panel correspond to the first spectra in each cycle of measurements, i.e., the spectrum numbers 1, 11, 21, and 31 in Fig. 6. The bias voltage applied to the sample during the MDS measurement was -25.8 V.

For more quantitative analysis, the cutoff positions of the spectrum are plotted as a function of the sample bias in Fig. 9. It is clear that the linear relation between the cutoff of the spectrum, E_{cutoff}, and the sample bias, V_{bias}, is obtained, and the least-square fitting revealed that this linear relation is given by $E_{cutoff} = 0.94|eV_{bias}| + 14.2$, where e is the elementary charge. The results confirmed

3.4. Measurement of ionization potential

As mentioned above, a MDS spectrum can provide the information on the ionization potential of insulators as that done by UPS [34,35]. The schematic of the measurement of the ionization potential of insulators by means of MDS is shown in Fig. 10. When primary He*

atoms are irradiated onto the insulator surface, an electron having the maximum energy in an MDS spectrum, which is emitted via the Auger de-excitation process, is that excited from the top of the valence band by receiving the residual energy of E_{1s-2s} corresponding to the energy difference between the 1s and 2s shells of He* and detected without any energy losses. An electron with the lowest energy is that emitted from the insulator surface having an energy close to the vacuum level at the insulator surface. Since the sample bias V_{bias} (<0) should be applied when the ionization potential is measured, the maximum energy, E_{max}, i.e, the cutoff energy of the MDS spectrum, is given as $E_{max} = E_{1s-2s} - eV_{bias}$. The minimum energy of the spectrum, E_{min}, i.e., the onset of the spectrum is given by $E_{min} = E_{ip} - eV_{bias}$. Therefore, the width of the MDS spectrum, E_{width}, is written by $E_{width} = E_{max} - E_{min} = E_{1s-2s} - E_{ip}$. Here, as mentioned in section 3.3, the energy scale should be corrected when the MDS spectrum is measured with the bias being applied to the sample. Thus, the ionization potential of insulators, E_{ip}, is determined from

$$E_{ip} = E_{1s-2s} - \left(E_{width}/0.94\right). \tag{1}$$

Here, E_{max}, E_{min}, and V_{bias} should satisfy 22 eV $\le E_{max} \le$ 41 eV, 22 eV $\le E_{min} \le$ 41 eV, and -28 V $\le V_{bias} \le$ -9 V, respectively.

   Note that, when the MgO surface is contaminated, there may be a contribution of the electron emission via the resonance ionization and Auger neutralization processes to the MDS spectra because the change in the electronic structure in the MgO surface might enable the resonant transition of a 2s electron in He* to the MgO surface to occur. After the resonance ionization of He*, this He ion is de-excited via the Auger neutralization process and an electron is emitted from the MgO surface as that explained at the text of Fig. 1. Under such a condition, the maximum energy of an electron in the MDS spectra is different from $E_{max} = E_{1s-2s} - eV_{bias}$ and given by $E_{max}' = E_{1s-2s} + E_{2s} - 2E_{ip} - eV_{bias}$, where E_{2s} is the binding energy of a 2s electron in He*. By comparing E_{max} and E_{max}', it is found that $E_{max} > E_{max}'$ is always satisfied for MgO because of $E_{2s} < 2E_{ip}$, confirming that the maximum energy of the MDS spectra is given by E_{max} and that E_{ip} can be determined using Eq. (1).
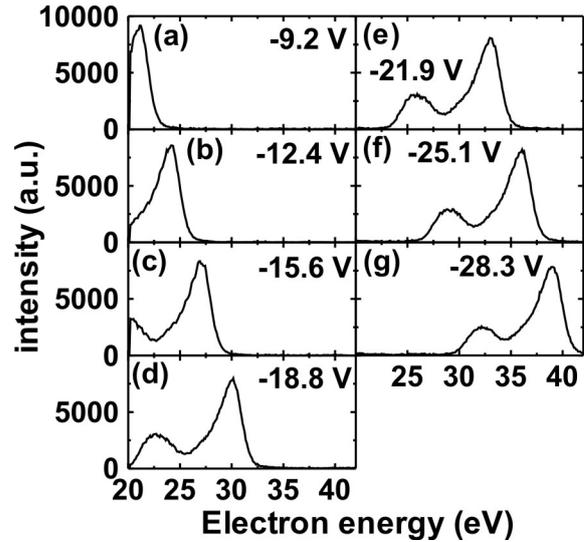

Fig. 8. MDS spectra for the MgO thin film of 50 nm thickness at different sample biases of (a) -9.2, (b) -12.4, (c) -15.6, (d) -18.8, (e) -21.9, (f) -25.1, and (g) -28.3 V. The measured range of the electron energy was 20 to 42 eV for all spectra.
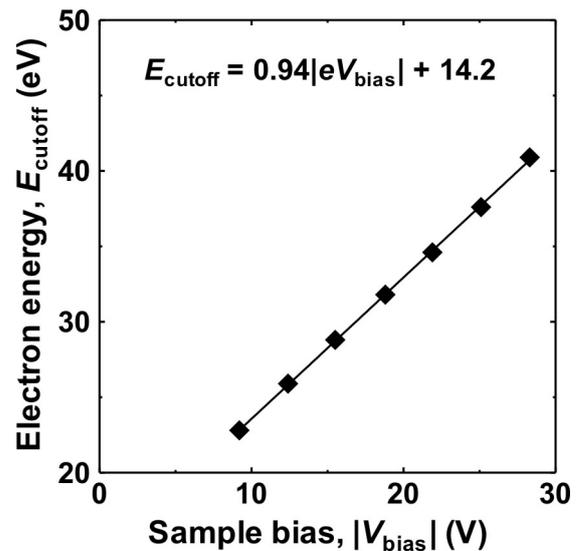

Fig. 9 Dependence of the cutoff energy of the MDS spectra on the sample bias determined from the spectra shown in Fig. 8. Solid line represents the least-square fitted equation. The cutoff energy was determined as the intersection of the straight line corresponding to the negative slope of the cutoff of the spectrum and the abscissa.

   In Fig. 11, the variation in the ionization potential, E_{ip}, of the MgO film of 50 nm thickness by heating treatment is shown by open circles. The values were determined from the MDS spectra shown in Fig. 3. It is found that E_{ip} is higher for the surface of the as-received MgO film.

By heating above 300°C in vacuum, E_{ip} decreases, and E_{ip} slightly increases for the clean surface. The change in E_{ip} might be attributed to the fact that contaminations on the as-received MgO surface are gradually removed by heating in ultrahigh vacuum, which significantly affects the electron emission process in MDS. The value of E_{ip} for the clean surface is found to be close to that estimated from the typical values of the band gap of $E_g = \sim 7$ eV and the electron affinity of $\chi = 0.9$ eV [36,37].
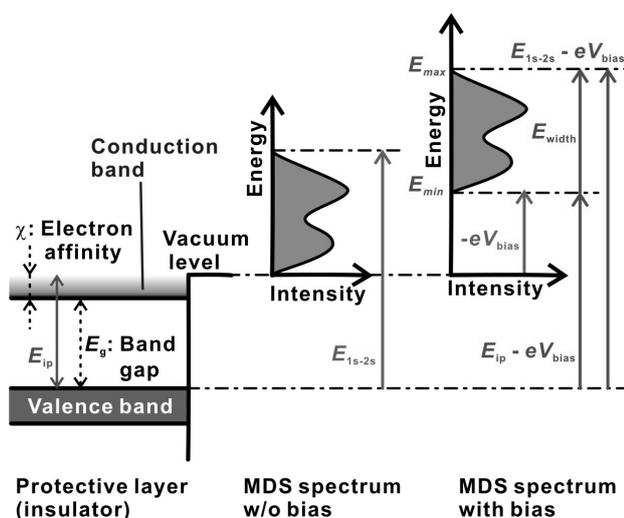
the as-received MgO film of 50 nm thickness was directly measured using pulsed-ion beam technique and specially designed secondary electron detector [38]. These findings revealed the correlation between the ionization potential, E_{ip}, measured by MDS and γ. The approach with the combination of MDS and the measurement of γ is found to be effective to elucidate the IISE phenomenon at the insulator surface.

Fig. 10. Schematic of the measurement of the ionization potential, E_{ip}, using MDS. E_{max} and E_{min} are the maximum and minimum energy of an MDS spectrum. E_{1s-2s} is the energy difference between the 1s and 2s shells of He* (19.8 eV). V_{bias} (<0) is the bias voltage applied to the sample during the MDS measurements.
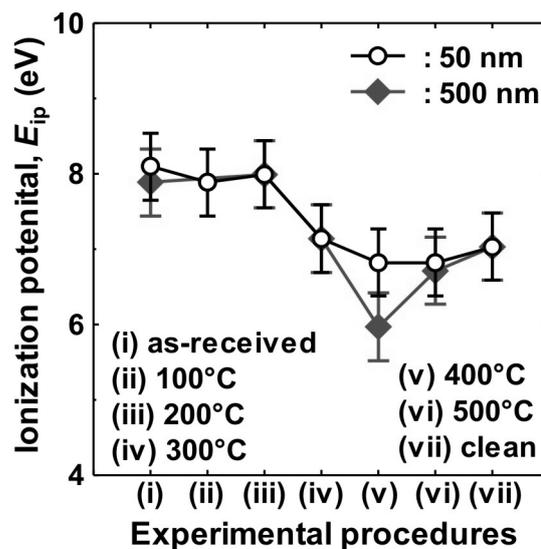

Fig. 11. Change in ionization potential, E_{ip}, of the MgO films of 50 (open circles) and 500 nm thicknesses (solid diamonds) induced by heating. The MDS spectra used for the determination of E_{ip} for MgO films of 50 and 500 nm thicknesses were those shown in Figs. 3 and 12, respectively. The experimental procedures are (i) the as-received surface and after heating at (ii) 100, (iii) 200, (iv) 300, (v) 400, (vi) 500°C, and (vi) the clean surface, respectively.

Note that the values of E_{ip} are largely affected by a longer tail at the cutoff and onset of the MDS spectra. The tail is significant for the as-received surface and after heating at the lower temperature as confirmed in Fig. 3. The longer tail in the MDS spectra might be attributed to the impurity and/or defect levels formed by contaminations on the MgO surface. The detailed investigation of effects of the absorption of possible contaminants on the MgO surface, such as H_2O, CO_2, and O_2, on the MDS spectra is underway. It should be also noted that the variations in the ionization potential shown in Fig. 11 suggests that the ion-induced secondary electron yield, γ, is increased by heating at the lower temperature and decreases for the clean surface. This tendency has just been confirmed by the authors, in which the variation in γ of

3.5. Dependence of MDS spectra on thickness of MgO film

Since the thickness of the MgO film used for PDPs is around 500 nm, MDS spectra for a MgO film of 500 nm thickness were measured and compared it with those for a 50 nm thick film, which was employed in the present study since charging during the MDS measurement is significantly reduced compared with that induced for a 500 nm thick film. Figure 12 shows the change in the MDS spectra of the MgO film of 500 nm thickness by heating. The heating procedures are the same as those done for the MgO film of 50 nm thickness shown in Fig. 3 except for heating at 100°C being skipped. The flux of

primary He* was the same as that used for the 50 nm thick MgO film in order to avoid charging. The peak at the higher-energy side shifts towards the higher energy with the increase in temperature. In addition, the intensity at the lower energy side decreases. These facts indicate that the MDS spectrum becomes close to that from the clean surface. These tendencies are similar to those observed for the 50 nm thick film in Fig. 3.
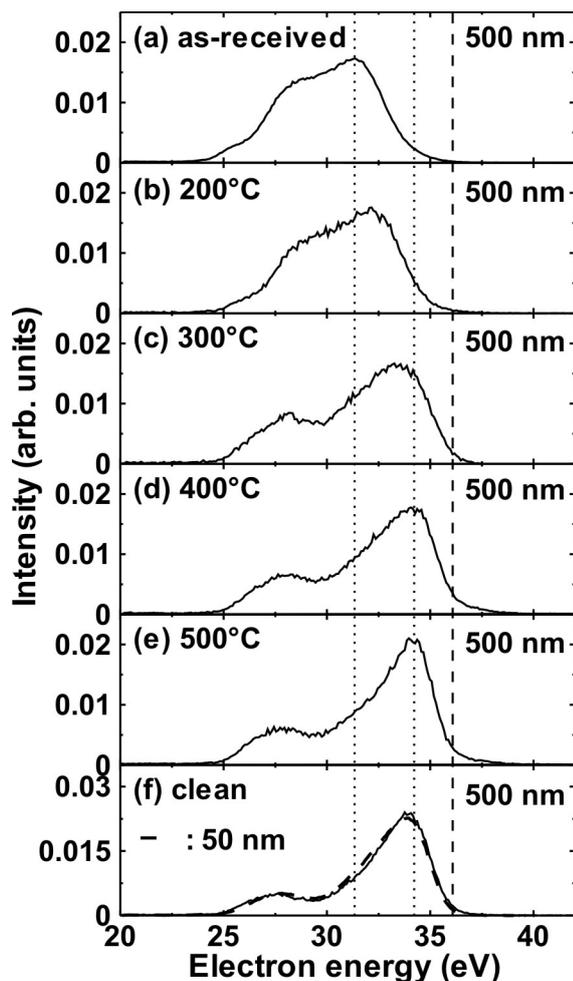

Fig. 12. MDS spectra of the MgO film of 500 nm thickness, the thickness of which is comparable to that used as the protective layer in PDPs. The experimental procedures are the same as those done for Fig. 3. (a) As-received surface, and after heating at (b) 200, (c) 300, (d) 400, and (e) 500°C in vacuum for one min at each temperature, and (f) the clean surface. For comparison, in (f), the MDS spectra of the clean MgO film of 50 nm thickness shown in Fig. 3(g) are also shown by thick broken line. The bias voltage applied to the sample during the MDS measurement was -24.6 V.

For comparison, the MDS spectra for the clean MgO film surface of the 500 nm thickness is shown in Fig. 12(f) and compared with that for the 50 nm thick film. It is found that the MDS spectra for the clean MgO film surfaces of 50 and 500 nm thicknesses are very similar, revealing that the 50 nm thick film is applicable to investigating the surface electronic structure of the MgO film used for PDPs.

For the further investigation, the values of E_{ip} determined for the 500 nm thick MgO film from Fig. 12 are shown in Fig. 11. A comparison with the results for the 50 nm thick film revealed that changes in E_{ip} with the increase in temperature is similar each other. The value of E_{ip} for the clean surfaces of the 50 and 500 nm thick MgO films are also similar, again confirming that the 50 nm thick film is useful for the investigation of the electronic structure of the MgO film used for PDPs. Note that the low flux of primary He* enables the measurement of the MDS spectra of 500 nm thickness without charging. However, the charging observed for the 500 nm thick MgO film is much significant than that for the 50 nm thick film, e.g., the observable charging was confirmed after the measurement of a couple of MDS spectra for 500 nm thick film. Therefore, in order to avoid effects of charging as much as possible, MgO films of 50 nm thickness were used for the investigation of the electronic structure using MDS.

4. Conclusions

In the present study, we investigated the measurement conditions of MDS applied to the MgO film used as a protective layer in PDPs. The present results are summarized as follows.

(i) The MDS spectra from the as-received MgO film of 50 and 500 nm thicknesses are changed by the heating treatment at 100 to 500°C in vacuum for one min. and becomes close to that from the clean surface. Although this heating treatment is effective to cleaning the MgO surface, this heating process is not sufficient to completely clean the MgO surface. For the cleaning, repeating sputtering by Ar+ ions and heating at 500°C is required.

(ii) The MgO surface is positively charged during the MDS measurement. Charging can be avoided by reducing the primary flux of He* to 1/1000 of that used in

conventional measurements. The irradiation of keV electrons is effective to remove positive charging induced during the MDS measurements. The neutralization is realized by the low-energy secondary electrons emitted by irradiation of keV electrons.

(iii) The MDS can be applied to the measurement of the ionization potential of the MgO film. The heating treatment of the as-received MgO film in vacuum induces the decrease in the ionization potential, E_{ip}. The variation in E_{ip} by heating was found to correlate with the change in γ.

The present results confirmed that MDS is one of the effective techniques to evaluate properties of MgO films used for PDPs. In addition, the investigation of the electronic structure of the MgO film by MDS and the measurement of γ is found to be effective to comprehensively understand the IISE emission mechanism from the MgO film. Further investigations of the change in the electronic structure and γ induced by the absorption of possible contamination onto the MgO film surface are underway and will be reported shortly.

5. Acknowledgment

6. References

[1] H. Uchiike, K. Miura, N. Nakayama, T. Shinoda, and Y. Fukushima, *IEEE Trans. Electron Dev*. **ED-23**, 1211 (1976).

[2] K. S. Moon, J. Lee, and K. W. Whang., *J. Appl. Phys.* **86**, 4049 (1999).

[3] H. S. Uhm, E. H. Choi, and J. Y. Lim, *Appl. Phys. Lett.* **80**, 737 (2002).

[4] T. Hirakawa, S. Goto, S. Zhang, and H. Uchiike, *Proc. International Display Workshops (IDW) '02* (Hiroshima, Japan, 2002) p. 749.

[5] Y. T. Matulevich and P. A. Zeijlmans van Emmichoven , *Phys. Rev.* B **69**, 245414 (2004).

[6] P. Riccardi, P. Barone, A. Bonanno, A. Oliva, P. Vetrò, M. Ishimoto, and R. A. Baragiola, *Nucl. Instr. and Meth.* B **230**, 455 (2005).

[7] Y. Motoyama and F. Sato, *IEEE Trans. Plasma Sci.* **34**, 336 (2006).

[8] J.-M. Jeoung, B.-D. Ko, H.-J. Lee, Y.-W. Jung, K.-W. Jung, S.-O. Kang and E. H. Choi, *Jpn. J. Appl. Phys.* **45**, 7901 (2006).

[9] Y. Morimoto, Y. Tanaka, and A. Ide-Ektessabi, *Nucl. Instr. and Meth.* B **249**, 440 (2006).

[10] Y. Cho, C. Kim, H.-S. Ahn, E. Cho, T.-E. Kim, and S. Hana, *J. Appl. Phys.* **101**, 083710 (2007).

[11] S. I. Ahn, H. Uchiike, S. E. Lee, K. Kim, and S. J. Kwon, *Jpn. J. Appl. Phys.* **46**, 6022 (2007).

[12] H. K. Kim, T. S. Kim, J. Lee, and S. K. Jo, *Phys. Rev.* B **76**, 165434 (2007).

[13] S. I. Ahn, S. E. Lee, S. H. Ryu, K. C. Choi, S. J. Kwon, and H. Uchiike, *Thin Solid Films* **517**, 1706 (2009).

[14] Y. Mizuhara, J. Kato, T. Nagatomi, Y. Takai and M. Inoue, *J. Appl. Phys.* **92**, 6128 (2002).

[15] T. Tsujita, T. Nagatomi, Y. Takai, Y. Morita, M. Nishitani, M. Kitagawa and T. Uenoyama, *Jpn. J. Appl. Phys.* **43**, L753 (2004).

[16] T. Tsujita, T. Nagatomi, and Y. Takai, *Surf. Interface Anal.* **37**, 137-140 (2005).

[17] T. Tsujita, K. Nakayama, T. Nagatomi, Y. Takai, Y. Morita, M. Nishitani, M. Kitagawa and T. Uenoyama, *J. Surf. Anal.* **12**, 284 (2005).

[18] T. Nagatomi, T. Kuwayama, Y. Takai, K. Yoshino, Y. Morita, M. Kitagawa, and M. Nishitani, *Appl. Phys. Lett.* **92**, 084104 (2008).

[19] T. Nagatomi, T. Kuwayama, K. Yoshino, Y. Takai, Y. Morita, M. Nishitani, and M. Kitagawa, *J. Appl. Phys.* **106**, 104912 (2009).

[20] K. Yoshino, T. Nagatomi, Y. Morita, T. Oue, N. Kosugi, M. Nishitani, M. Kitagawa, and Y. Takai, *Jpn. J. Appl. Phys.* **49**, 040212 (2010).

[21] K. Yoshino, T. Nagatomi, Y. Morita, T. Oue, N. Kosugi, M. Nishitani, M. Kitagawa, and Y. Takai, *Jpn. J. Appl. Phys.* **49**, 086205 (2010).

[22] K. Yoshino, T. Nagatomi, Y. Morita, T. Oue, N. Kosugi, M. Nishitani, M. Kitagawa, and Y. Takai, *Jpn. J. Appl. Phys.* **50**, 026201 (2011).

[23] H. D. Hagstrum, *Phys. Rev.* **96**, 336 (1954).

[24] H. D. Hagstrum, *Phys. Rev.* **122**, 83 (1961).

[25] Y. Motoyama, H. Matsuzaki, and H. Murakami, *IEEE Trans. Electron Dev.* **48**, 1568 (2001).

[26] M. Kurahashi and Y. Yamauchi, *Surf. Sci.* **420**, 259 (1999).

[27] M. Yoshitake, *J. Surf. Sci. Soc. Jpn.* **28**, 397 (2007)

Journal of Surface Analysis Vol.18, No. 1 (2011) pp. 13−25
K. Yoshino et al. Investigation of Measurement Conditions of Metastable De-excitation Spectroscopy of MgO
Thin Films Used for Plasma Display Panels

[in Japanese].

[28] K. G. Eyink, B. C. Lamartine, and T. W. Haas, *Appl. Surf. Sci.* **21**, 29 (1985).

[29] I. Ogoh, R. Shimizu, and H. Hashimoto, *Jpn. J. Appl. Phys.* **24**, 1145 (1985).

[30] Y. Mizuhara, J. Kato, T. Nagatomi, Y. Takai, and M. Inoue, *Jpn. J. Appl. Phys.* **42**, L709 (2003).

[31] Y. Mizuhara, T. Bungo, T. Nagatomi, and Y. Takai, *Jpn. J. Appl. Phys.* **44**, 6289 (2005).

[32] Y. Ueda and H. Kurokawa, *J. Vac. Soc. Jpn.* **45**, 97 (2002) [in Japanese].

[33] H. K. Hwang, C. H. Jeong, Y. J. Lee, Y. W. Ko, G. Y. Yeom, *Surf. Coat. Technol.* **177 –178**, 705 (2004)

[34] F. Bebensee, F. Voigts, and W. Maus-Friedrichs, *Surf. Sci.* **602**, 1622 (2008).

[35] F. Voigts, F. Bebensee, S. Dahle, K. Volgmann, and W. Maus-Friedrichs, *Surf. Sci.* **603**, 40 (2009).

[36] W. H. Strehlow and E. L. Cook, *J. Phys. Chem. Ref. Data* **2**, 163 (1973).

[37] J. Dresner, *J. Appl. Phys.* **48**, 4760 (1977).

[38] Y. Murasawa, J. Azargal, K. Yoshino, T. Nagatomi, Y. Takai, Y. Morita and M. Nishitani, 5th International Symposium on Practical Surface Analysis and 7th Korea-Japan International Sumposium on Surface Analysis (PSA-10) (Gyeongju, Korea, October 3-7, 2010) p.176.

査読コメント
査読者 1．山田健二（石川工業高等専門学校）

　AC 型 PDP の放電電圧を下げるためにγ作用を活性化させる課題は重要であります．本研究は，表面最外層電子状態に敏感な MDS 法を利用して，この課題解決に結びつく MgO 膜への帯電やイオン化ポテンシャルについて研究したもので重要な貢献であると考えます．以下に質問を示します．

[査読者 1-1]

　Abstract で，keV 電子照射によって放出された 2 次電子の再分布による中和化，とはどういう意味でしょうか．実験データあるいは参考文献をお示しください．

[著者]

　この点に関しては，「3.2. Charging during MDS measurement and neutralization by high-energy electron

irradiation」の第 2 段落の後半と第 3 段落の最後に記述があり，引用文献は[17]です．この文献 [J. Surf. Anal. **12**, 284 (2005)] をご指摘の通り，アブストラクト中に引用いたしました．

[査読者 1-2]

　確認として，Low Flux で帯電しないのは total の Flux が低いためで，照射回数を増やすと low Flux でも帯電効果が表れるということでしょうか．このコメントとして，17 ページ，左，下から５行目からの説明が位置付けられるのでしょうか．

[著者]

　ご指摘の通りです．誤解を招かないために「 without observable charging during successively measuring a few MDS spectra,」という文章を該当箇所（17 ページ左カラム下から 4-2 行目）に追加いたしました．

[査読者 1-3]

　３ｋeV の電子線照射でプラスの電荷を取り除けることが示されていますが，マイナスに帯電することはないのでしょうか．

[著者]

　MgO 膜の膜厚が 50 nm のため，3 keV 電子を照射した領点では電子線誘起伝導（electron-beam induced conduction）が生じて電荷が膜を抜けられる条件が成立しており，照射点近傍には電子線照射によって電荷は蓄積されない状態です．照射点から放出された 2 次電子が, 照射点の周りの He^*照射によって表面が正に帯電している部分の正のポテンシャルを感じて二次電子が再配分されて正帯電が中和されます．これらについては文献[17. J. Surf. Anal. **12**, 284 (2005)]に詳細に議論されております．XPS 等で用いられる中和銃と同様の条件が成立していると考えられます．

　この点を明確にするために，以下の文章を「3.2. Charging during MDS measurement and neutralization by high-energy electron irradiation」の第 2 段落の中ほど（17 ページ右カラム 7-10 行目）に追加いたしました．

　「The electron irradiation itself does not induce charging because of the so-called electron-beam induced conduction since the range of primary electrons exceeds the film thickness [17]」

[査読者 1-4]

Fig.11 で，なぜ heating によってイオン化ポテンシャル Eip が減少したのでしょうか．表面のコンタミネーションによる RI+AN の脱励起プロセスが，Eip の減少に関係していませんか．

[著者]

ご指摘の通りです．ありがとうございます．最終的な清浄 MgO 表面では，Fig. 2 のところで述べている通り，共鳴準位が存在しないために AD が支配的になります．ただし酸素欠陥なども存在すると想定されるため 100%AD であるとは言えませんが，MDS のピーク形状等と一般的な MgO の状態密度から，RI+AN よりも AD に近いと判断しています．これに対して as-received の試料では表面に汚染等が存在するため RI＋AN 過程も起こっていると考えており，それが Fig. 3 の MDS スペクトルの形状変化として現れています．結果，加熱の過程での Eip の変化は，当然，表面汚染の脱離過程で表面の電子状態が変化したことを反映していると考えております．

こで「3.4. Measurement of ionization potential」の最後から 2 段落目の中ほど(21 ページ左カラム 3 行目)に以下の文章を追加いたしました．

「The change in EIP might be attributed to the fact that contaminations on the as-received MgO surface are gradually removed by heating in ultrahigh vacuum, which significantly affects the electron emission process in MDS.」

[査読者 1-5]

Fig. 11 と 12 で，50nm と 500nm の帯電で差異はないとの結果ですが，そうすると両者の帯電において表面の何が関係していると考えられるのでしょうか．

[著者]

500 nm の MgO 膜についても 50 nm と同様の He* フラックスを用いて，さらに MDS スペクトルを 1 本測定するごとに帯電を緩和しているため，帯電の影響が殆ど見えておりません．しかしながら実際には，500 nm の方がはるかに帯電しやすく，MDS スペクトルを数本測定すると帯電の影響が見られます．そのため 500 nm の場合は，表面状態の変化等によって帯電の影響がより現れてしまう場合も考えられます．そこで，MDS による評価という点では 50 nm と 500 nm で差がないため，帯電の影響を 500 nm に比べてより排除できる 50 nm で測定を行っています．

そこで「3.5. Dependence of MDS spectra on thickness of MgO film」の第一段落（22 ページ左カラム 1-3 行目）に以下の文章を追加しました．

「The flux of primary He* was the same as that used for the 50 nm thick MgO film in order to avoid charging.」

さらに「Results and Discussion」の最後（「4. Conclusions の直前」）に以下の文章を追加いたしました．

「Note that the low flux of primary He* enables the measurement of the MDS spectra of 500 nm thickness without charging. However, the charging observed for the 500 nm thick MgO film is much significant than that for the 50 nm thick film, e.g., the observable charging was confirmed after the measurement of a couple of MDS spectra for 500 nm thick film. Therefore, in order to avoid effects of charging as much as possible, MgO films of 50 nm thickness were used for the investigation of the electronic structure using MDS.」