Measurement of Energy Band Structure of MgO, MgSrO and MgCaO Thin Film by their Secondary Electron Emission Coefficient due to Auger Neutralization

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Abstract. The energy band structure of MgO, MgSrO and MgCaO thin films has been investigated based on the Auger neutralization theory. Profiles of secondary electron emission from MgO, MgSrO and MgCaO thin films have been measured by gamma focused-ion-beam ($\gamma$-FIB) system. We have measured the energy band structure, $f_\alpha(\alpha)$, function in their respective valence band from the secondary electron emission characteristics by $\gamma$-FIB system with He ion beam whose energy is less than 200 eV in the surface of MgO, MgSrO and MgCaO thin films. For this work, we have employed a Fast Fourier Transform (FFT) and its Inverse-Fast Fourier Transform of the secondary electron current profile emitted from the thin films due to the Auger neutralization mechanism for the determination of the energy band structure $f_\alpha(\alpha)$.

1. Introduction

Nowadays the trend of display industry today is going to the three-dimensional (3D) image system, where plasma display panel (AC-PDP) and liquid crystal display (LCD) are the major players in the world display markets. It is known that the AC-PDP has the better response time and the color impression than the LCD panel, because the visible color light is noticeably comfortable reducing eyestrains. In order to lower the firing voltage in AC-PDP, a high emission coefficient ($\gamma$) of the secondary electrons from the protective layers like CaSrO film [1-2] is needed. However, this CaSrO is extremely sensitive to H$_2$O and CO$_2$, forming hydroxides and carbonates of Ca and Sr. It is therefore necessary to avoid exposure of deposited CaSrO protective layers to atmosphere by processing the PDP front glasses in inert gases or vacuum [3]. Hence we propose the MgSrO and MgCaO thin film for the protective layers for AC-PDP, in which small amounts of strontium Sr and calcium Ca are included in the MgO pellet, respectively, in this research. Therefore it is essential and necessary to evaluate the material properties of MgSrO and MgCaO whether these materials could be used for protective layer instead of conventional MgO film and also can be used for the alternative material for CaSrO in AC-PDP.

In this experiment, we have compared characteristics of MgO, MgSrO and MgCaO thin films by X-ray diffraction pattern (XRD) and secondary electron emission coefficient ($\gamma$). The measurement of electron energy band structure of MgO single crystal is one of the essential factors to improve the efficiency in AC-PDP, in which the work-function ($\phi_w$), energy band width $\chi$, central energy $\epsilon_0$ of the valence band and any other important information of MgO thin film are also accordingly analyzed and obtained. The work function $\phi_w = E_{i0}/2$ of specified MgO thin film has been experimentally obtained from the direct

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measurement of ion-induced secondary electron emission co-efficient $\gamma$ versus the various ionization energies $E_i$ for slow ions and its extrapolation of least-squared-fitting for determinations of $E_{i0}$, which is the ionization energy satisfying the zero emission of ion-induced secondary electrons. During the measurement of the work function $\phi(w)$ of MgO thin film from the ion-induced secondary electron emission co-efficient $\gamma$, the slow ions of He$^+$, Ne$^+$, Ar$^+$, N$_2^+$, and Xe$^+$, whose energy is less than 100 eV have been used throughout the experiment [4]. We have investigated the respective electron energy band structure of MgO, MgSrO and MgCaO thin films, using the results of secondary electron emission characteristics ($\gamma$) based on the Auger neutralization by gamma focused-ion-beam ($\gamma$-FIB) system.

2. EXPERIMENTAL CONFIGURATIONS

Figure 1 shows a schematic of the $\gamma$-focused ion beam (FIB) system consisted of the thermal electron source, the ionization region of ions, the electrostatic single Einzel lens that focused the ion beam, and the collector and copper pad for the measurement of the secondary electron emissions from the surface of the thin films.

![Figure 1. Schematic view of the $\gamma$-FIB system.](image-url)
The thin films of MgO, MgSrO and MgCaO have been deposited by electron beam evaporation at 300℃ and evaporation speed of 20 Å/sec, where their thicknesses are about 6000~8000 Å in this experiment. We have employed the He ion whose ionization energy E_i is 24.58 eV with low energy below 200 eV in this experiment. The He ion approaches the surface of film material, as shown in the figure 1. It is noted that the electric field is polarized toward the collector from the grounded copper pad when the collector potential is negative biased. The secondary electrons emitted from the surface by this slow ion then come back, and only the ion current (I_i) coming to the surface is then measured. On the other hand, the positively biased collector makes the electric field toward the grounded copper pad. Due to this electric field, the secondary electrons emitted from the surface of thin film by the ion beam bombardment move up toward the collector, registering the current (I_t) in the ampere meter shown in the figure 1, in which the emitted secondary electron and ion beam currents (I_i) are included together. The secondary electron emission \( \gamma \) is obtained from \( \gamma = (I_t - I_i) / I_i \) [5].

Figure 2 shows the schematic diagram for the Auger neutralization. When an ion approaches on the surface of the respective MgO, MgSrO and MgCaO thin film, an electron in the valence band is combined to the approaching ion by quantum mechanical tunneling effect for their neutralization and this ion becomes to be dropped to the ground state. During the neutralization process, the energy for tunneling electron for neutralization has been transferred to the nearby electron. When the transferred energy to the nearby electron is higher than the work-function, then the secondary electrons could be emitted from the surface at the vacuum. We define the characteristic energy spread of electrons in the valence band as \( \chi \) and energy level located in the center of the valence band as \( \varepsilon_0 \), which is shown in figure 2. The symbol \( \alpha_{\text{min}} \) for an electron in figure 2 is the work function of respective MgO, MgSrO and MgCaO thin film and we defined as \( \alpha_{\text{min}} = \varepsilon_0 - (\chi / 2) \), \( \alpha_{\text{max}} = \varepsilon_0 + (\chi / 2) \), and also \( \beta \) for nearby electron is similar to that for \( \alpha \). If minimum kinetic energy \( E_k^{\text{min}} \) from the electrons located at \( \alpha_{\text{max}} \) and \( \beta_{\text{max}} \) is almost close to zero, we can set \( E_k^{\text{min}} = (E_0 - \chi) / 2 \) [4].

The Auger transform \( T(E_k) \) defined as

\[
T(E_k) = \frac{1}{\chi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_\varepsilon(\beta) \delta(E_k - E_i + \alpha + \beta) f_\varepsilon(\alpha) d\alpha d\beta
\]  

For convenience in the subsequent analysis, the dimensionless energy variables \( x \) and \( x' \) are defined as \( x = (\alpha - \varepsilon_0) / \chi \) and \( x' = (\beta - \varepsilon_0) / \chi \), where \( \chi \) is the characteristic energy spread of electrons in the valence band. Then, Eq. (1) is equivalently expressed as \( x' = y - x \), where the energy variable \( y \) is defined by

\[
y = \frac{E_i - 2\varepsilon_0 - E_k}{\chi}
\]  

The state density function \( f_\varepsilon \) in the valence band is a function of the electron energy \( \alpha \) in the band. The Auger transform \( T(E_k) \) defined by Eq. (1) could be expressed by

\[
T(E_k) = \frac{1}{\chi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_\varepsilon(\beta) \delta(x' - y + x) f_\varepsilon(\alpha) d\beta d\alpha
\]  

The 15th International Conference on Thin Films (ICTF-15) IOP Publishing
Journal of Physics: Conference Series 417 (2013) 012009 doi:10.1088/1742-6596/417/1/012009
Now the $T(E_k)$ function can be expressed in terms of variables $y$ and $x$ as

$$T(y) = \int_{-\infty}^{\infty} f_e(x) f_e(y-x) dx.$$  \hspace{1cm} (4)

For a specified density $N(E_k)$ of final states, the Auger self-convolution $T(y)$ in Eq. (4) can be experimentally determined from

$$T(y) = \frac{N_0(E_k)}{N(E_k)}$$

by measuring the distribution in energy, $N_0(E_k)$, of electrons escaping from the thin film. It is noted that the Auger self-convolution for ultra-thin film may have the same profile as the distribution of electrons in energy because of 2-dimensional structure. The Auger self-convolution $T(y)$ in Eq. (4) is a typical convolution of the state density function $f_e(x)$ in the valence band. It is convenient in the subsequent analysis to define the Fourier transform by

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \exp(ikt) dt,$$  \hspace{1cm} (5)

Taking the Fourier transform of both sides in Eq. (4), it is straightforward to show that the Fourier transform $S(k)$ of the Auger self-convolution $T(y)$ in Eq. (4) relates to the Fourier transform $F(k)$ of the normalized density function $f_e$ by

$$S(k) = \sqrt{2\pi} \left[ F(k) \right]^2.$$  \hspace{1cm} (6)

Finally, the state density function $f_e$ in the valence band could be obtained by using the inverse-FFT (IFFT) of $F(k)$, i.e.,

$$f_e(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{-ikx} dk$$  \hspace{1cm} (7)

Hence we will have the information of the density-of-state function of $f_e(x)$ in the valence band of thin film surfaces of MgO, MgSrO and MgCaO [4].
3. RESULTS AND DISCUSSIONS

The thin films of MgO, MgSrO and MgCaO have been deposited by electron beam evaporation under the 10⁻⁵ Torr working pressure and the gas temperature 300 °C. Figure 3 shows the top and side images of MgO, MgSrO and MgCaO thin films at the upper and lower sides, respectively, by scanning electron microscopy (SEM). The surface shapes of MgO and MgCaO are shown to be triangular with columnar structure of (111) crystal orientation. On the other hands, the surface image of MgSrO has shown to be smoother than others, and shown to be without any crystal orientation. Thicknesses of MgO, MgSrO and MgCaO thin films are about 780nm, 640nm and 740nm, respectively. It is noted that the MgO, MgSrO, and MgCaO films have been deposited by pure MgO pellet, MgSrO pellet doped with 15% strontium, MgCaO pellet doped with 10% calcium, respectively, in this experiment.
Figure 3. The top (upper) and side images (lower) of MgO, MgSrO and MgCaO thin films by scanning electron microscopy (SEM).

Figure 4 shows the X-ray diffraction pattern of the MgO, MgSrO and MgCaO thin films, in which MgO and MgCaO shows the poly crystallinities of (111), (200) and (220). Also it is noted that there is no crystal orientation for the MgSrO thin film. It has been found that the MgCaO thin film has an obvious peak of (111) orientation, by which the secondary electron emission coefficient ($\gamma$) might be generated higher than others.
Figure 4. X-ray diffraction pattern of MgO, MgSrO and MgCaO thin films deposited by E-beam evaporation.

Figure 5 shows the secondary electron emission coefficients ($\gamma$) from MgO, MgSrO and MgCaO thin films, which have been measured by gamma FIB system, versus the He ion energy ranged from 130 eV to 200 eV.

Figure 5. Secondary electron emission coefficient ($\gamma$) of the MgO, MgSrO and MgCaO thin films.
It is shown that the secondary electron emission coefficient ($\gamma$) for MgCaO thin film has the highest value over He ion energy of 160 eV since it has poly crystalline orientation of (111) and (220), as shown in figure 4. It is noted that the secondary electron emission coefficients ($\gamma$) for MgO, MgSrO, and MgCaO thin films are 0.054, 0.059, and 0.061, respectively, under He ion energy of 200 eV. When a He$^+$ ion approaches on the MgO, MgSrO, and MgCaO thin films, the secondary electron is released to outside of these thin film surfaces by Auger neutralization theory and the pico-ammeter measures this released electron. We have measured the current signals with respect to the collector voltage in the $\gamma$-FIB system, represented by the solid square-dot in figures 6(a), 7(a) and 8(a) for the MgO, MgSrO, and MgCaO thin films. These current signals have been captured by using a pico-ammeter connected to the grounded copper pad in figure 1, where the collector voltage was swept from -8 V to +15 V, with resolution of 0.1 V.

(a) Secondary electron current vs. collector voltage  
(b) Plots of Auger transform $T(E_k)$ vs. $E_k$

Figure 6. Secondary electron emission current versus collector voltage (a) and plot of Auger transform $T(E_k)$ in terms of the secondary electron kinetic energy $E_k$ emitted from the MgO thin film

(a) Secondary electron current vs. collector voltage  
(b) Plots of Auger transform $T(E_k)$ vs. $E_k$

Figure 7. Secondary electron emission current versus collector voltage (a) and plot of Auger transform $T(E_k)$ in terms of the secondary electron kinetic energy $E_k$ emitted from MgSrO thin film
The energy distribution for the emitted secondary electron from the film surfaces could be represented by differentiating the current signal with respect to the collector voltage. It is noted that the emitted electrons has maximum kinetic energy at the low collector potential corresponding to the current starting--up, but it has a minimum at the collector potential around 11V corresponding to current saturation point, as shown in figures 6(a), 7(a) and 8(a). Rescaling this electron distribution in terms of the electron kinetic energy, we can experimentally obtain the Auger transform $T(E_k)$ defined in Eq. (1). The Auger transforms of $T(E_k)$ have been plotted for the thin films of MgO, MgSrO, and MgCaO in figures 6(b), 7(b) and 8(b), respectively, in terms of the their electron kinetic energy, in which the characteristic energy spread $\chi$ of electrons in the valence band could be measured since the energy spread for the secondary electrons are denoted by $2\chi$ and the center of the valence band $\varepsilon_0$ could be estimated by $\varepsilon_0 = (E_i - \chi)/2$. Making use of the Auger transform for $T(E_k)$, which is the energy distribution profiles for the emitted secondary electrons, as shown in figures 6(b), 7(b) and 8(b), and carrying out the Fourier transform and inverse transform numerically as mentioned in Eqs. (6) and (7), the electron energy band structures, i.e., density-of-state function $f_d(\alpha)$, of the thin films can be obtained by Eq. (7).
Figure 9 shows the electron energy band structure, i.e., the density of state function for the electrons in valence band in MgO, MgSrO, and MgCaO thin films, where the work function $\phi_w$ and the center of the valence band $\varepsilon_0$ in the valence band are represented, respectively. It is noted that the work functions $\phi_w$ are found to be about 7.1 eV, 6.9 eV, 6.4 eV for MgO, MgSrO, and MgCaO thin films, respectively. Also the central energies $\varepsilon_0$ of valence band are found to be about 9.7 eV, 9.6 eV, and 9.4 eV for MgO, MgSrO, and MgCaO thin films, respectively. It is also noted in this experiment that the kinetic energy spread, which is given by $2\chi$, of the emitted secondary electrons are 10.5 eV, 10.9 eV, and 11.8 eV for MgO, MgSrO, and MgCaO thin films, respectively. From these data, the MgCaO thin film could be used for the best protective layer for the AC-PDP in comparison with other MgO and MgSrO films since the work function $\phi_w$ and the central energy $\varepsilon_0$ of the valence band are minimum values for the highest value of the secondary electron emission coefficient.

4. CONCLUSIONS

The electron energy band structure $f_s(\alpha)$ of the MgO, MgSrO and MgCaO thin films has been investigated, respectively, under the Auger neutralization theory by measurement of the secondary electron emission current emitted by low energy He ion beam whose energy less than 200 eV with the gamma focused ion beam ($\gamma$-FIB) system. Making use of the Auger transform for $T(E_0)$, which is the energy
distribution profiles for the emitted secondary electrons, and its inverse Fourier transform yield the state
density function \( f_s(\alpha) \) of MgO, MgSrO, MgCaO in the valence band. MgCaO is found to have the highest
secondary electron emission coefficient \( (\gamma) \) for He ion energy in the range of 130 eV and 200 eV. It is also
noted that MgCaO film has the lowest central energy \( \varepsilon_0 = 9.4 \) eV and the work function \( \phi_w = 6.4 \) eV.
Therefore, our experimental observation indicates that MgCaO thin film looks like to be the most efficient
material for emission of the secondary electron, which will in turn eventually reduce the firing voltage and
provide a high brightness in plasma display panel.

ACKNOWLEDGEMENT
This research was supported by the MKE (The Ministry of Knowledge Economy), Korea under the
ITRC (Information Technology Research Center) Support Program supervised by the NIPA (National IT
Industry Promotion Agency)” (NIPA-2009-C1090-0902-0018) and also supported by the SRC program
(20100029418). This work also partially supported by Kwangwoon University 2012.

5. REFERENCES
[1] Motoyama Y, Kurauchi T, 2006 SID 06 Digest, 1384
[2] Matulevich Y T et al, 2007 IMID 07 Digest, 213
[3] Matulevich Y T et al, 2009 IMID 09 Digest, 181-183
[4] Uhm H S, Choi E H, and Cho G S, 2009 Appl. Phys. Lett. 94, 0031501
[5] Lim J Y, Oh J S, Ko B D, Cho J W, Kang S O, Cho G S, Uhm H S, Choi E H, J. Appl. Phys. 2003 94, 764
[6] Choi J H, Son C G, Hong Y J, Park B J, Uhm H S and Choi E H, ADVANCES IN
NATURAL SCIENCES : Nanosci. Nanotechnol. 2010 1, 045014, 5