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Ion-induced secondary electron emission, optical and hydration resistant behavior of MgO, Mg–Mo–O and Mg–Ce–O thin films

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ABSTRACT

Optical transmittance, hydration resistance and secondary electron emission characteristics of e-beam evaporated pure and Mo- or Ce-containing MgO thin films have been investigated. While the increased grain size and pyramidal columnar morphology following incorporation of molybdenum and cerium in MgO are responsible for the excellent discharge characteristics, emergence of neutral {100} and {110} MgO surfaces preferentially give rise to high optical transmittance (~92–100%) and stability against hydration. Further, addition of Mo (or Ce) in MgO causes significant increase in defect density which, in turn, enhances the photoluminescence (PL) emission from 5-, 4- and 3-coordination sites. The changes lead to lowering of the breakdown voltage and hence improvement in the secondary electron emission (SEE) efficiency. These facts have been supported by ion-induced SEE yield (γ) deduced from the a.c. breakdown voltage observed, taking neon as a discharge gas, and determined semi-empirically as well with Hagstrum's theory based on Auger neutralization process using (i) band offset parameters and surface band gap data derived from X-ray photoelectron spectroscopy signal and (ii) information of defect energy levels obtained from photoluminescence (PL) measurements. The experimental values of neon ion-induced SEE yield (γ) are found to be 0.35, 0.42 and 0.39 for MgO, Mg–Mo–O ($x = 0.035$) and Mg–Ce–O ($x = 0.01$) thin films, respectively.

1. Introduction

Lead-rich glass is quite suitable for dielectric layer in plasma display panels (PDPs). It exhibits low melting point, high optical transmittance, low temperature coefficient of expansion, and excellent discharge characteristics. However, the inert gas ions, electrons, photons, and meta-stable atoms present in PDPs decompose PbO into Pb + $1/2O_2$. Also, the binding energy of PbO is poor, which makes reverse reaction constant '$[Pb][O_2]^{1/2}/[PbO]$' very small. Thus, it is difficult to maintain adequate stability of the dielectric layer [1]. MgO is a potential candidate for protecting the glass dielectric layer and improving the overall characteristics [1,2]. Hence, in addition to its conventional application as a chemically stable buffer layer for high temperature superconductor and ferroelectric thin films [3–5], MgO has received attention in plasma display panels (PDPs). It protects the glass against erosion and displays high ion-induced secondary electron emission and low plasma firing voltage [6–19]. The technological needs related to reduction of power consumption for full high definition (full-HD) performance and single scanning of address driving circuits highlight further the importance of high secondary electron emission (SEE) yield (γ) [20]. The elements like strontium, zinc, zirconium, calcium, aluminum, and titanium have been incorporated in MgO [21]. Due to low ionization energy and reasonable anionic vacancy generation capacity, titanium/zirconium containing MgO exhibits excellent secondary electron emission properties [22]. Molybdenum and cerium can be equally useful as their oxidation state(s) are comparable and their first three ionization energies are even lower than titanium and zirconium (Table 1 [23]).

The characteristics of protective layers are determined by SEE yield γ, which itself depends on electron affinity, work function, energy band gap and intra-band levels [20,24–28]. Since the protective layers are insulators in nature, the charging phenomenon makes the precise measurements of γ difficult. Hence, an attempt has been made here to deduce γ values semi-empirically using photoluminescence data and Hagstrum's theory [20,24,25,29,30], and by measuring firing voltage with possible minimization of the charging effect as well.

2. Experimental details

Pure MgO powder has been synthesized first by a sol–gel process using magnesium nitrate hexahydrate and oxalic acid as precursors and ethanol as a solvent. The process essentially involves gel formation, drying at 100 °C for 24 h to yield magnesium oxalate dihydrate and its decomposition to MgO at 600 °C for 2 h. The product is then subjected

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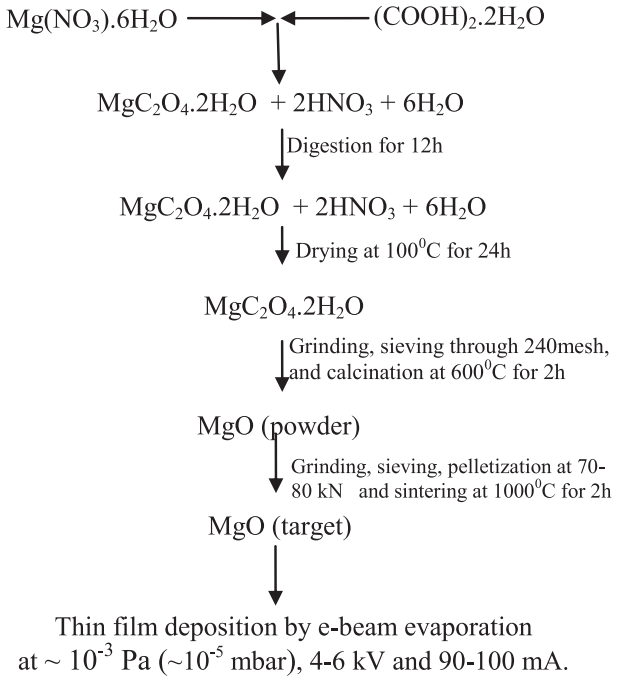
Table 1
Oxidation state(s), ionic radius (in six coordination) and ionization energies of zirconium, titanium and cerium.

Element	Oxidation state(s)	Ionic radius (Å)	Ionization energies (kJ/mol)		
			First	Second	Third
Zr	4	0.720	640.1	1270.0	2218.0
Ti	4 (2, 3)	0.605 (0.86, 0.67)	658.8	1309.8	2652.5
Ce	4 (3)	0.870 (1.01)	534.4	1050.0	1949.0
Mg	2	0.72	737.7	1450.7	7732.7
Mo	6 (3, 4, 5)	0.73 (0.69, 0.65, 0.61)	684.3	1560.0	2618.0

to grinding, sieving through a 240 mesh, pelletization at a hydraulic pressure of 70–80 kN, and sintering at 1000 °C for 2 h to obtain a MgO target. Thin films of MgO have been prepared over the clean glass, quartz, ITO coated glass, and silicon substrates by e-beam evaporation under vacuum ~10^{-5} mbar (0.001 Pa) using emission current of 90–100 mA at ~4–6 kV. The flowchart showing steps involved in preparation of MgO thin films is given in Scheme 1. Similar procedure has been adopted to prepare thin films of molybdenum- or cerium-containing MgO (termed as Mg–Mo–O or Mg–Ce–O, and defined by Mo/(Mo + Mg) for Mg–Mo–O and Ce/(Ce + Mg) for Mg–Ce–O) by taking appropriate amount of ammonium heptamolybdate tetrahydrate or cerium nitrate hexahydrate precursor as well at the initial stage of powder synthesis.

The crystallographic nature of thin films has been evaluated by X-ray diffraction using a Thermo Electron model ARL X'TRA diffractometer with CuKα_1 radiation (wavelength $\lambda = 1.54056$ Å). An atomic force microscope (Molecular Imaging model PicoSPM) has been used for observing the morphology and determining the surface roughness. In addition, a Fourier transform infrared spectrometer (Bruker model Vertex-70), a UV–vis spectro-photometer (Hitachi model U-3310), and a spectro-fluorophotometer (Varian Cary Eclipse) have been employed for the detection of –OH bond, measurement of optical transmittance, and recording of the photoluminescence (PL) spectra, respectively. An X-ray photoelectron spectrometer (VG-Microtech Multilab) equipped with a hemispherical electron analyzer and a 150 W MgKα ($h\nu = 1253.6$ eV) radiation source has been utilized to determine energy band offsets. For this, thin films have been mounted on



Scheme 1. The flowchart of steps involved in preparation of MgO thin films.

stainless steel stubs with double sided conducting carbon tape and put in an air lock area at a pressure of $\leq 10^{-5}$ Pa (~10^{-7} mbar) for ~10 h before transferring to the main analysis chamber. Upon achieving residual pressure of 10^{-8} Pa (~4×10^{-10} mbar), XPS spectrum was drawn from the data collected at the takeoff angle of 45° with a step of 0.2 eV using pass energy of 20 eV. The experimental values of the ion-induced secondary electron emission coefficient (γ) have been obtained using a set-up designed and developed in the laboratory during the course of investigation (details given in Section 3.6).

3. Results and discussion

3.1. Phase and microstructure

The X-ray diffraction (XRD) pattern of MgO thin film (thickness ~500 nm) prepared by e-beam evaporation on the glass substrate revealed the formation of a stable periclase phase (f.c.c., NaCl-type) with two strong peaks centered at 2θ positions of 42.78 and 62.07° corresponding to 200 and 220 reflections, respectively (fig. not shown here due to brevity). This indicates <100> and <110> preferred orientations of the MgO thin film. The lattice parameter as determined from the Bragg angle of 200 diffraction peak is 4.225 ± 0.005 Å (known bulk value being 4.213 Å [JCPDS #04-0829]). Mg–Mo–O and Mg–Ce–O thin films also show similar crystallographic orientations for the prevailing periclase-type phase in each case.

Fig. 1 shows a few atomic force microscopic images of MgO, Mg–Mo–O and Mg–Ce–O thin films obtained at a scan rate of 2.1 lines per second using a cantilever with a force constant of 4 N/m at a resonance frequency of 159 kHz. These exhibit pyramidal columns of different heights. The preferential growth is caused by variation in the sticking coefficient and mobility of adatoms perhaps. However, the growth process is relatively suppressed in samples containing higher amounts of Mo/Ce additive. The film growth appears to follow Volmer–Weber mechanism (i.e., 3D island growth) [31]. The columnar grains of triangular shapes are known to show excellent discharge characteristics [32]. The value of root mean square (rms) roughness of thin films has been obtained using the expression given by El Feninat et al. [33]. The rms roughness values are 4.0 nm (MgO), 83.9 and 10.1 nm (Mg–Mo–O; x = 0.035 and x = 0.35) and 61.2 and 6.1 nm (Mg–Ce–O; x = 0.01 and 0.10). It means addition of molybdenum or cerium at low levels has profound effect on the surface roughness and causes significant improvement in tendency of columnar growth. This feature increases the life time, stabilizes the discharge and, in turn, enhances the display quality of PDPs [34].

3.2. Evaluation of band offsets and intra-band levels

X-ray photoelectron spectroscopy (XPS) has been used to determine the valence and conduction band offset parameters. In case of MgO, the electron mean free path (λ) becomes just ~1 nm if the kinetic energy gained from Mg Kα radiation is taken as ~1253.6 eV; $\hbar w_p$ being 22.7 eV with $\hbar$ = Planck's constant and w_p = plasmon frequency [35]. Thus, XPS signals associated with no energy loss emanate from the surface region and provide information about the species present there. Moreover, the charging phenomenon affects the position and not the nature of signal in the XPS spectrum. Hence the density of states (DOS) determined by the peak width remains preserved and can be used to estimate band offsets to yield the SEE-γ values. Several XPS spectra were collected to obtain the valence band offsets as signal lacked in resolution. The spectra have been examined carefully in each case for making the measurement (shown by two arrows in Fig. 2 for illustration) and averaged for obtaining the information of valence band offset. Although, these band offsets are coarse estimates, they demonstrate the variation trends of γ well. Even though the measured XPS line widths are the convolution of the X-ray signal, the natural line