International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2014 Vol. 4 (1) January-March, pp. 117-123/Sabnis
Research Article

MANUFACTURING MgO SLIM FILMS FOR IMPROVED MORPHOLOGY, CRYSTALLINE STRUCTURE AND DEPOSITION RATE BY MODIFIED SQUIRT PYROLYSIS METHOD

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ABSTRACT

Quality MgO slim films can be effectively organised by ultrasonic squirt pyrolysis procedure on Si (1 0 0) base. The microstructure and electrical properties of the deposited MgO slim films were explored by X-ray diffraction (XRD), scanning electron microscopy (SEM) Results specified that the MgO slim films display island growth characteristic at relatively lower deposition temperature and sheet growth characteristic at higher temperature. Highly (2 0 0) sloping MgO films with standardised and impenetrable surface and extremely high resistivity can be realised under the enhanced circumstances of Ts = 680^{O}C, which makes it suitable as a buffer layer for the succeeding development of focused ferroelectric materials.

INTRODUCTION

MgO films can be used as buffer coating for the deposition of high Tc superconducting films and perovskite-type ferroelectric films (Fork *et al.,* 1991). MgO slim films are settledas a guarding layer of dielectrics to advance the release characteristics and the panel's lifespan in a plasma display panel (Urade *et al.,* 1976). At the moment, a few studies onthe growth of MgO films are done using chemical vapour deposition method (Kwak *et al.,* 1989; Desisto and Henry, 1990). The principal complications in the deposition of MgO slim films using chemical vapour deposition are extraordinary cost and small deposition rate. However, the squirt pyrolysis method has numerous advantages, such as comparatively small cost, easy configuration control, big zone deposition, and great growth rate. Its drawback is the difficulty of controlling the droplet size because large droplets could be harmful to the deposition of high quality films. The electrostatic squirt pyrolysis method has been normally used to produce nano-sized specks of oxidic materials (Zomeren *et al.,* 1994) adapted the squirt pyrolysis method to the electrostatic squirt deposition technique and successfully deposited LiMn2O4 slim films using the electrostatic squirt deposition technique. Several oxide slim films including ZnO (Ryu and Kim, 1995) LiCoO2 (Chen *et al.,* 1996) and SrBi2Ta2O9 (Han *et al.,* 1997) have been deposited by this method. MgO slim films have been widely used as a chemically unwavering buffer layer for the deposition of high Tc superconducting films and perovskite-type ferroelectric films because of its noble lattice matching with revealed materials and low chemical reactivity (Gurvitch and Fiory, 1987). Many ferroelectric and superconducting oxide films, such as PZT, $LiNbO_3$, $BaTiO_3$ and $YBa_2Cu_3O_7$, etc., (Desisto and Henry, 1991) are prepared on Si substrates, using MgO as a transitional layer. Furthermore, MgO has the benefits of a wide band gap, low optical loss, and a moderately low refractive index that licences narrowed optical modes in ferroelectric materials. Freshly, MgO slim films have also been functional as shielding layers of dielectrics to surge the discharge characteristics and the panel's lifespan in a plasma display panel (Kim *et al.,* 2000). Quite a few methods for the preparation of MgO films and coatings have been developed during the last few years, such as pulsed laser deposition (PLD), magnetron sputtering, electron beam evaporation, metal organic chemical vapour deposition (MOCVD), and squirt pyrolysis (Ishiguro *et al.,* 1996; Shih*et al.,* 1991; Talacchio *et al.,* 1989; Lu *et al.,* 1993; Yi *et al.,* 1996). Ultrasonic squirt pyrolysis has freshly arose as a flexible deposition process capable of fabricating high quality oxide and sulphide slim films (Lee *et al.,* 2001). The Ultrasonic squirt pyrolysis procedure is established on the thermal decomposition of the source solution squirted by an ultrasonic nozzle onto the heated substrate exterior. Paralleled with other deposition systems, the ultrasonic squirt pyrolysis technique retains the benefit of minimalism, low equipment cost, high deposition rate and good thickness standardization over a large area. In this study, high quality MgO slim films have been successfully deposited by the ultrasonic squirt pyrolysis, and the characteristics of gained MgO films were studied by XRD, SEM and SRM. The development mechanisms of MgO films deposited at altered temperature are discussed. The physical properties, electrostatic squirt pyrolysis particularly the microstructure and morphology, of the electrostatic squirt deposited slim films were strongly related to the deposition process parameters, such as the diameter of the nozzle, substrate-to-nozzle space, kind of precursors, and solvents. However, the electrostatic squirt deposition method can be modified to increase the morphology of the electrostatic squirt deposited slim films. In a modified electrostatic squirt pyrolysis system, which has been developed and espoused in this study, an abstraction electrode, guide, and guide heaters were added to the conventional electrostatic squirt pyrolysis system to reduce the size of droplets and to augment the vaporization of solvent in the droplets during flight to the substrate. In this work, high quality MgO slim films were efficaciously deposited and categorised.

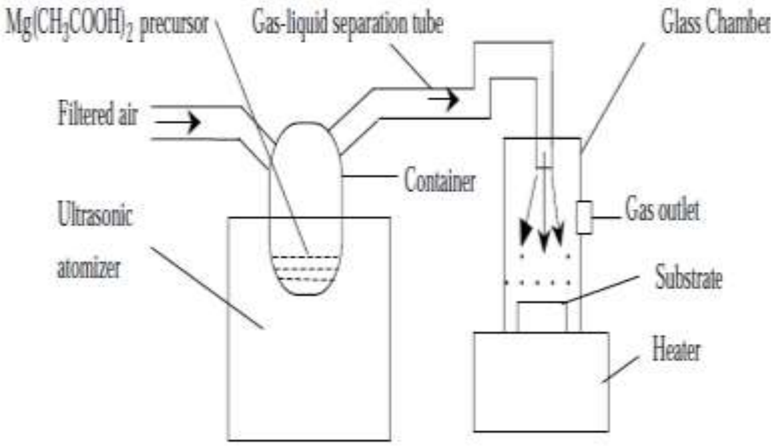

Figure1: Schematic diagram of the modified electrostatic squirt pyrolysis system

Experiments

A graphic illustration of the amended electrostatic squirt pyrolysis system is exemplified in Figure1. One grounded ring-shape extraction electrode was introduced between the nozzle and the substrate to increase the electric-field strength. The high voltage, 14 kV, applied between the stainless-steel nozzle and the chastised extraction electrode created sub-micrometer-sized droplets at the end of the nozzle. The applied voltage formed a multicone-jet, which consisted of several emitting cone jets around the tip ofthe capillary. The higher the electric field strength, the smaller the droplets formed at the tip of the nozzle (Robinson *et al.,* 1980), the number of jets being increased with increasing applied voltage (Clouteau and Prunet-Foch, 1994). This is possible because of the multicone-jet mode to concurrently find a large number of Taylor cones and, consequently, comparatively elevated flow rates (Wilson, 1982). A guide, which had a cylindrical shape, was hosted between the nozzle and the substrate and was heated by a pair of guide heaters. As a result, the flow of released droplets was dedicated and the evaporation of the solvent and the decomposition of precursor were also improved throughout the voyage of the emitted droplets to the substrate through a guide. Therefore, the deposition of constant and thickly chockfull MgO slim films could be realised by the modified electrostatic squirt pyrolysis system with a guide heater. A liquid precursor was equipped by dissolving 0.5 M magnesium acetate (Mg (CH3COO)$_2$_4H_2O) aqueous solution was selected as a precursor solution in the solvent; the acetic acid played a role to prevent the foundation from being oligomerized in the solvent. The flow rate of the liquid precursor was kept at 7.9 ml per hour. The MgO films were deposited on 500 A° thick Si (100) substrates, the size being 25 x 25 mm^2, at various substrate temperatures(Ts) and escort temperatures (Tg). Both temperatures were restrained at the middle of the substrate surface and the guide outer surface, electrostatic squirt pyrolysis correspondingly. To eliminate protracted surface oxides, the substrates were etched with diluted HF

(15%) just before the deposition. The substrate was set on a stainless steel plate and heated to desired temperature of 580, 630 and 680 **^{O}C** for sample A, B and C, correspondingly. An ultrasonic atomizer was casted off to attain a soft, low-velocity squirt and unvarying spreading of micrometer-sized droplets. The subsequent aerosol is consequently elated to the substrate to form the desired MgO slim films. After the removal, the films were galvanised at 720**^{O}C** in oxygen for 12 min to decrease the crystalline flaws and sequester the enduring organic matter, which consequences in well-crystallized structure. By wavering the time of deposition at different substrate temperature, MgO films with almost the same thickness of 200 nm were prepared. The MgO films are characterized using X-ray diffraction (XRD). For the structural analysis, scanning electron microscopy (SEM) for the analysis of surface morphology, and X-ray photoelectron spectroscopy(XPS) for the determination of the binding states of elements.

RESULTS AND DISCUSSIONS

Figure 2 shows the resilient enslavement of the growth rate on substrate and guide temperatures. It designates that at Tss580 ^{O}C, 630 ^{O}C and 680^{O}C the development rate augmented with cumulative Tg. At these substrate temperatures, the instigation energy was estimated to be 53 kJ/mol. The growth rate, however, decreased at 580^{O}C because of source depletion initiated by a homogeneous reaction, consequential in a coating of white particles on the guide wall. The XRD spectra for the MgO films deposited at various Ts are shown in **Figure 2.**There was no extraordinary necessity of orientation and peak intensity on Tg. From the XRD result, the lattice parameter was calculated which is very close to thatof a pure Single Crystal of MgO. It also indicated that the MgO films were deposited witha (100) favoured alignment, irrespective of the substrate temperature. In addition, it showed that the MgO slim films deposited at higher Ts had better crystallinity than those at lower Ts, even though they were slenderer due to a lower deposition rate. The reason is that adsorbed atoms mobility on a film surface was enhanced at higher Ts, so that Mg and O atoms with a higher mobility on the surface could easily move to equipoise atomic sites, i.e. the (100) plane, resulting in a (100) favoured alignment. It is commonly recognized that the (100) plane in MgO has a lower surface energy than the (110) and (111) Planes (Rayleigh, 1992). The degree of a (100) favoured alignment and the perceptiveness of the (100) peak in the XRD pattern of MgO slim films deposited at 580^{O}C by the adapted electrostatic squirt pyrolysis method seem analogous to those of the MgO slim films which weredeposited using a b-diketonate precursor at temperatures as high as 630 ^{O}C by chemical vapour deposition (Kwak *et al.*, 1989) or annealed at temperatures overhead 700^{O}C after squirt pyrolysis deposition (Desisto and Henry, 1990).Figure 4 shows SEM micrographs of MgO films deposited at various Ts, evidently demonstrating that MgO slim films deposited for all of the deposition environments were dense, while the surface roughness of the films upsurges with accumulative Ts. As shown in Figure3, a number of large particles were disseminated on the surface of the films deposited at

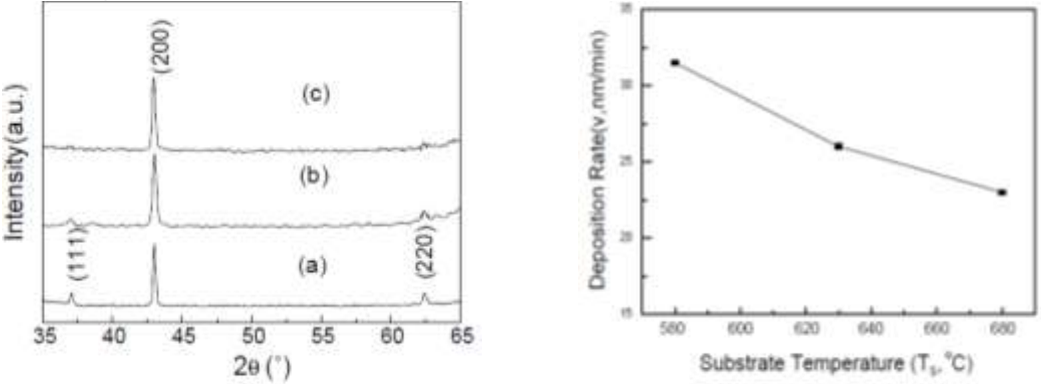

Figure2: Variation of deposition rate at various substrate temperatures(Ts) as a function of Deposition rate, X-ray diffraction patterns for MgO films deposited a different substrate temperatures: (a) 580 ^{O}C; (b) 630 ^{O}C; (c) 680 ^{O}C

high Ts of 580 ^{O}C Since a guide was heated, the solvent in a solution droplet was evaporated during the flight of a droplet. The evaporation rate for small volatile droplets can be intended by using Equation 1 (Hinds, 1982; Chen *et al.,* 1996) where d is the droplet diameter; D is the diffusion coefficient of the vapour of the solvent in air; M is the molecular mass of the solvent; R is the gas constant; ris the compactness of the solution; P is the partial vapour pressure of the solvent away from the droplet; Pd is the partial vapour pressure at the droplet surface; T is the ambient temperature; Td is the droplet temperature which is customarily<T due to cooling by evaporation; and λ is the mean free path of air. The evaporation of the solvent resulted in the reduction of the droplet, keeping the total amount of charge the same (Abbas and Latham, 1967). A charged droplet may be disrupted into a few smaller droplets, after attainment of an extreme attainable charge density, q_R, for a liquid droplet with radius d. This is the so-called Rayleigh limit (Rayleigh, 1992), which is expressed in Equation 1.

$$\frac{q_R}{m} = \frac{q_R}{4\pi d^3 \varrho/_3} = \frac{6}{\varrho}\left[\frac{\Upsilon \mathcal{E}_0}{d^3}\right]^{1/2} \text{------ Equation 1}$$

Where m is the mass of the droplet; g is the surface tension of the liquid with reverence to the neighbouring gas; and $\mathcal{E}_0$ is the absolute permittivity of free space.The commotion of a droplet typicallytranspires with theexpulsion of a few exceedingly charged, very trivial droplets. According to Equations 1, the emitted droplet snomadic from the nozzle to the substrate were evaporated and interrupted, and accordingly their size befitted smaller. The evaporation rate of the reduced droplets augmented with substrate temperature. After the solvent in a droplet was totally vaporised, the decomposition rate of the Mg precursor in a droplet increased with the temperature, too. Hence, large MgO particles occurred by homogeneous nucleation before the Mg gas phase source arrived on a substrate, or on a film surface in the case of a film deposited at 680 ^{O}C compared with films at 580 to630 ^{O}C. As a result, the large particles on the film surface are shown in Figure3.

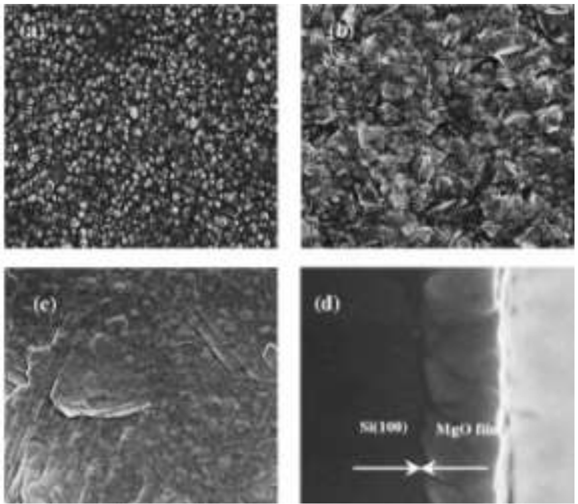

Figure 3: SEM micrographs of MgO films deposited at: (a) Ts = 580 ^{O}C; (b) Ts = 630 ^{O}C; and (c) Ts=680 ^{O}C; (d) is a low magnification of (c). The guide temperature(Tg) was kept at 200 ^{O}C for all films

It is well known that H_2O and CO_2 molecules are easily chemisorbed onto MgO surfaces and form Mg $(OH)_2$ and $MgCO_3$(Scamehornet al.,1994). After sputtering for 3 minutes, only the peak from oxide at 546 eV remained; that from the Mg $(OH)_2$was completely removed after 2 min of sputtering.In addition, the air-exposed MgO slim film showed two C 1s peaks at 287 eV and 291 eV from CO and CO_2, correspondingly, which appeared to be chemisorbed during the acquaintance in air. These peaks vanished after 3minutes of sputtering of the surface of the MgO slim film. Hence, the chemisorbed CO and

CO_2particles on the exterior were easily removed, and a few C atoms were also assimilated in the MgO slim film from the b-diketonate precursor during installation.

Deposition Rate

It can be established that the deposition rate shrinkages with the upsurge of Ts, notwithstanding the fact that the kinetics of MgO establishing reaction intensification with cumulative temperature. The experimental dependency can be enlightened by the reduced mass transport to the substrate at higher temperature due to gas convection from the substrate pushing the droplets of the precursor away. Moreover, the diminution of film deposition rate is also related to the increase of the film density with increasing temperature. The higher diffusion energy supplied by the higher temperature is considered to be beneficial for the particles to fill in the internal defects, which results in the formation of denser films. Similar results have been reported by authors (Krunks and Milikov, 1995; Fu *et al.*, 1999).

Crystalline Structure

From the results of X-ray diffraction analysis various conclusions about the MgO films deposited at various Ts can be drawn. It can be seen that the MgO films with (2 0 0) preferred orientation were formed. With the increases of Ts, the (2 0 0) diffraction peak becomes progressively more dominant. At the deposition temperature of 680 8C, the film are strongly textured with preferential orientation along the (2 0 0) axis. The observed relationship between the degree of (2 0 0)-preferred orientation and the deposition temperature may be explained in terms of the migration of molecules onto the growing surface. MgO is expected to achieve a (2 0 0) preferential orientation that has a lower energy configuration during nucleating. The absorbed Mg and O atoms with a higher mobility enhanced at higher Ts could easily move to equilibrium atomic sites on the surface, i.e. the (2 0 0) plane of MgO which is energetically stable (Rayleigh, 1992) .Thus, the increase of (2 0 0) preferred orientation occurs while the substrate temperatureis enough high.

Morphology

SEM images of MgO films deposited at various Ts are shown in the figure D. It can be clearly seen that the morphologies of film exterior are strappingly reliant on the substrate temperature. For sample A, the quasi-spherical grains with a middling diameter of 85 nm are intermittently amassed with a rough surface. This asymmetrical accumulation of grains can also be observed on sample B, with accumulative grains diameter to 120 nm, less roughness and a few small pores, which was deliberated to be fashioned throughout the removal of organics. For sample C, an obvious alteration in surface morphologies can be observed. The surface exhibits layer morphology, and no observable defects over the substrate. The SEM image of the cross-section for sample C shows an enormously smooth and dense layer of MgO film with a thickness of 200 nm. It can be clinched from the above results that the growth mechanism of MgO film is pretentious strongly by substrate temperature. It can be connected with the change of deposition modes for the squirt pyrolysis method, which depends on the substrate temperature and the distance between the nozzle and substrate (Krunks and Milikov, 1995). For the MgO films deposited around 580 ^{O}C, it is possible that the droplet of Mg (CH3COO) $_2$_4H_2O evaporates before it scopes the substrate surface and the stemmed precipitate invades onto the surface where decomposition occurs. This is a typical Arrhenius behaviour in which the deposition rate is restricted by the assorted chemical reaction kinetics process at or near the substrate surface (Stryckmans *et al.*, 1996). The films develop faster in perpendicular direction than in parallel direction because of the high deposition rate and low migration of the enthralled molecules on a growing surface under the deposition mode. As a result, the film presents the characteristics of island growth mechanism and the MgO films with irregular or edge-like grains are observed with this growth mechanism. Whereas, for the deposition at a relative high temperature of 680 ^{O}C, the droplet of Mg (CH3COO) $_2$_4H_2O evaporates to form solid particles as it approaches the substrate surface, and the particles melts and vaporizes. Then, the solid vapour diffuses to the substrate to undergo a heterogeneous reaction there. This is the typical process in which the deposition rate is mass transport controlled (Rayleigh, 1992).The reaction kinetics is so fast that the surface reaction finally becomes controlled by mass transfer of the reactant. The films unveil the features of layer growth mechanism because of the low deposition rate and high migration of the absorbed molecules on a growing surface in this deposition mode. MgO films with smooth and dense surface and almost perfect (2 0 0) favoured alignment were attained with the appliance. This is the finest deposition ailment for high quality films. The growth mechanism for sample deposited at 630 ^{O}C is a evolution growth stage between the two mechanisms.

Conclusions

MgO slim films with high (2 0 0) favoured alignment and extraordinary resistivity were effectively deposited on Si(1 0 0) by ultrasonic squirt pyrolysis technique using magnesium acetate as source material. The typical characteristics of island growth and layer growth mechanism were observed at deposition temperatures of 580 and 680 ^{O}C, respectively. The dependence of film microstructure and micrograph on substrate temperature can be explained in terms of deposition modes and growth mechanism. High quality MgO slim films may be attained through the control of deposition modes and growth mechanism for the squirt pyrolysis method. Results show that our MgO films deposited at the optimal condition (680 ^{O}C) have considerable better excellence than those in previous squirt pyrolysis research. The MgO slim films with this quality should be suitable as a buffer layer for the succeeding growth of oriented ferroelectric material.

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