Preferred Orientation of MgO Films Prepared by Plasma-Enhanced Metalorganic Chemical Vapor Deposition

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Abstruct Thin films of magnesium oxide (MgO) with NaCl-type structure were prepared on Si(100) substrate at temperatures ranging from 300 to 600℃ by plasma-enhanced metalorganic chemical vapor deposition (PE-MOCVD) using magnesium dipivaloylmethanate (Mg-DPM) as a source material. At the substrate temperature 300 and 400℃, highly (220) oriented MgO films were obtained at lower O_2 flow rate. The increase in O_2 flow rate, orientation of MgO films changed from (220) to (200). And amorphous MgO films were prepared at O_2 flow rate above 20 cm^3 / min. At the substrate temperatures 500 and 600℃, highly (111) oriented MgO films were obtained at lower O_2 flow rate, and further increase in O_2 flow rate, (220) and (200) oriented MgO films were prepared in order as the increase in O_2 flow rate. (100) and (111) oriented films had columnar structure.

Key words: Magnesium oxide, MO-CVD, Thin film, Buffer layer

Introduction

There has been increased interest in rroelectric oxide thin films for their potential lvantages in technological applications. These cide films grown epitaxially and properly oriented :e favored for their advantages in using ferro-ectric, piezoelectric, nonlinear electro-optic, and her properties. The majority of thin film research r the growth of epitaxial films has been performed 7 using single-crystal oxide substrates because of ieir chemical properties and crystal structure. owever, interest in the growth of oxide-based evices on semiconductors has recently let to the use ' oriented MgO films to provide a chemically stable iffer layer.[1-3]

There have been many reports on the pitaxial growth of MgO on GaAs with several orientation relations including cube-on-cube.[1,4] Also, considerable works[5-13] have been carried out to grow textured MgO on Si substrate. To date, growth of textured MgO films has been carried out by using pulsed lase deposition,[5,6] electron beam evaporation,[7,8] reactive rf magnetron sputtering,[9] and chemical vapor deposition (CVD) [10-13] methods. In the CVD method, magnesium acetylacetonate, magnesium β -diketonate and magnesium 2-ethylhexanoate have been used as source material. Since these source materials have lower vapor pressure, they have to be heated above 200℃ or higher in order to obtain suitable deposition rate. This makes the reproducible preparation of MgO films difficult, i.e., vapor of source material was often condensed in transporting gas line.

In the present study, Mg-DPM is first

proposed as source material for preparation of MgO thin films by PE-CVD method. Because the complex have lower vaporization temperature of 140℃ and stable in air. The deposition of MgO films was studied under various O_2 flow rates at the substrate temperatures ranging from 300 to 600℃. The textures of the films on Si(100) substrate are discussed.

2. Experimental

A conventional cold wall type CVD apparatus equipped with inductively coupled rf plasma coil was employed in the present experiment. A quartz-tube reactor (78 mm in diameter) was placed horizontally, and the substrate was horizontally positioned on substrate holder in which a shell-shaped resistive heating element was placed. MgO thin films were deposited on Si(100) from Mg-DPM by a PE-MOCVD technique. Mg-DPM vapor was created by heating 0.2g of the complex by an auxiliary heater held at 150°C and transported to just above the substrate surface with argon gas through a gas line maintained at 180℃. Argon was used as the transporting gas. And oxygen as the oxidation gas was separately introduced into the reactor. The flow rates of argon transporting gas and oxygen oxidation gas were constant at 10 cm^3/min and from 0 to 50 cm^3/min, respectively. Then plasma was generated in the reactor at the rf power 100W. The deposition was mainly carried out for 30 min on Si(100) substrate at a total pressure of 10 Pa. The native oxide on substrate surface was etched with 20% HF solution prior to the deposition. The substrate temperature was measured with an alumel-chromel thermocouple located very close to the rear side of the substrate surface. Typical deposition conditions of the present study are summarized in Table 1.

After the deposition, the thin films with 300nm to 1500nm in thickness were examined by θ -2 θ type X-ray diffraction (XRD) using Cu K α radiation. Surface morphologies of thin films were observed by scanning electron microscopy (SEM). The thickness of the films was measured by a stylus profilometer.

Table 1. Typical deposition condition

Vaporrizing temperature	150℃
Ar flow rate	10 cm^3/min
O_2 flow rate	0~50 cm^3/min
Substrate Temperature	300~600℃
Rf power	100 W
Deposition pressure	10~35 Pa
Deposition time	30 min

3. Results and Discussion

Figure 1 shows the deposition rate of the films under various O_2 flow rates. The deposition rate decreased rapidly as the O_2 flow rate increased. The results may indicate that the rate determine step of the film formation was not the reaction of Mg-DPM with O_2 on substrate surface but was Mg or MgO_x elements to arrive on substrate surface. The increase in O_2 flow rate result in the increase in the probability of collision of Mg element and O_2 in vapor phase, in other words, a rapid decrease in the deposition rate might be caused by homogeneous nucleation of MgO in the vapor phase.

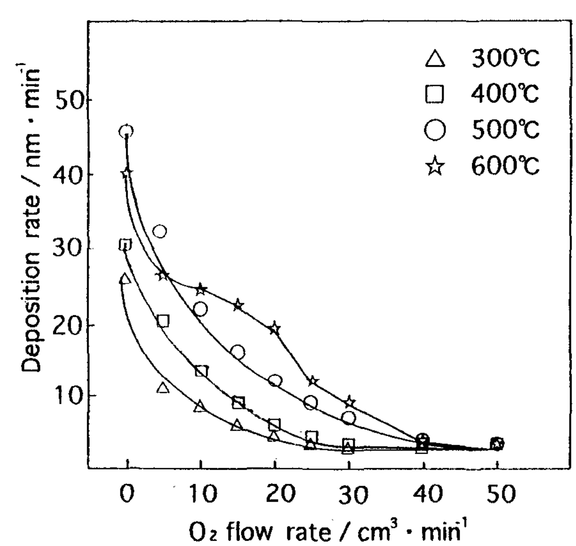

Fig. 1. Effect of O_2 flow rate on deposition rate of MgO films at various substrate temperatures.

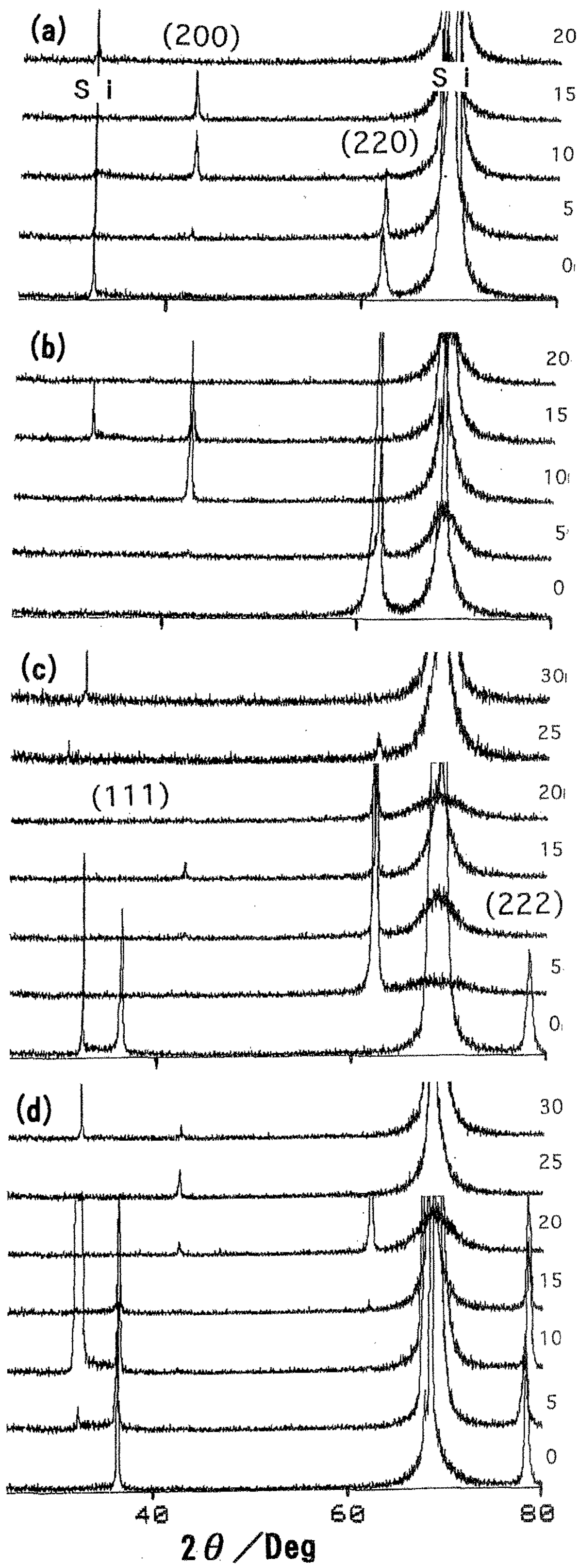

Fig. 2. XRD patterns of MgO films grown on Si(100) with various O_2 flow rate at substrate temperatures (a) 300℃, (b) 400℃, (c) 500℃, and (d) 600℃.

Figure 2 shows the XRD patterns of MgO films grow on Si(100) under various O_2 flow rates at substrate temperatures ranging from 300 to 600℃. At the substrate temperature 300℃, only (220) reflection due to (110) orientation was observed for MgO grown without O_2 flow. Increase in O_2 flow rate at 10 cm^3/min, mainly (200) reflection due to (100) orientation was observed, and only (200) reflection was observed at 15 cm^3/min. Further increase in O_2 flow rate resulted in a growth of amorphous MgO films. At the substrate temperature 400℃, similar growth tendency was observed for MgO films grown with various O_2 flow rates. At the substrate temperature 500℃, however, only (111) and (222) reflections due to (111) orientation were observed for MgO films grown without O_2 flow. And mainly (220) oriented MgO films were obtained under O_2 flow rate at 5, 10, and 15 cm^3/min. Further increase in O_2 flow rate resulted in poor crystallinity of MgO and lead to amorphous structure. At the substrate temperature 600℃, only (111) and (222) reflections were observed under O_2 flow rate 0 to 10 cm^3/min. And (220) and (200) reflections are observed in order as increase in the O_2 flow rate. To date, textured MgO films grown by CVD have been reported to be (100) and (110) oriented films. (100) and (110) oriented films tend to grow under higher and lower O_2 flow rates, respectively.[12] At a low deposition rate, sufficient migration may occur to form the (100) plane of MgO which is energetically stable. Similar growth tendencies were observed in the present experiments. (111) oriented films were first prepared by CVD methods in the present experiments. (111) oriented films were grown only at a high deposition rate. At a high deposition rate, insufficient migration tends to form the energetically unstable (111) plane of MgO, which has lower atomic density than the (100) and (110) planes. However, we have no idea why (111) oriented films tend to form at high temperatures such as 600℃. At higher substrate

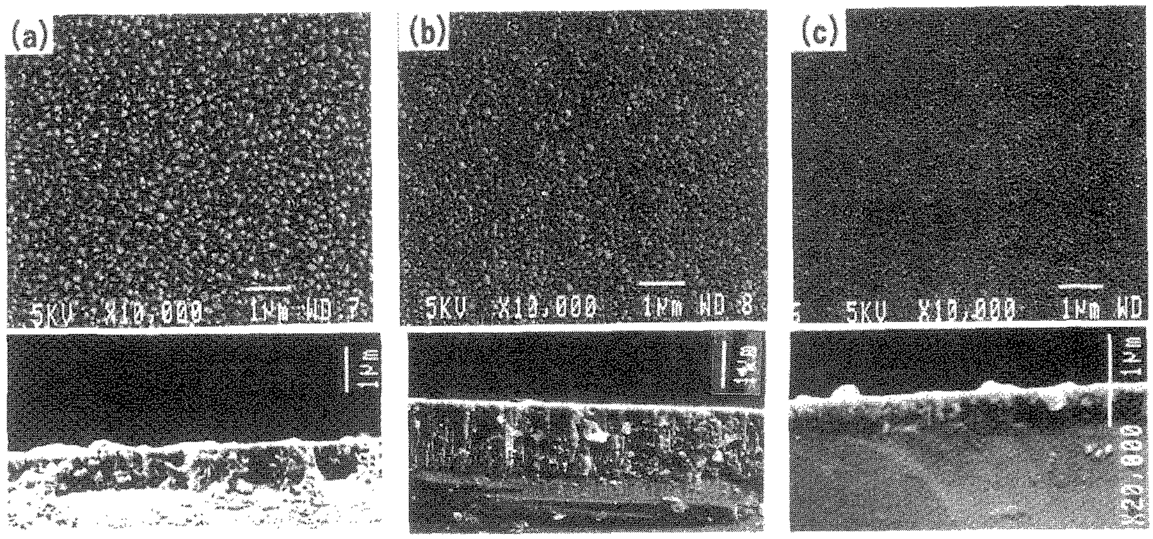

Fig. 3. SEM photographs of surface and cross sectional views of MgO. (a) (100) oriented, (b) (111) oriented, and (c) amorphous films.

temperatures, sticking coefficient of oxygen ion on SiO substrate surface may decrease. And Mg layer may formed as Si-O-Mg. Then oxygen ions were adsorped on Mg layer by electrostatic force to form Si-O-Mg-O bonding. Thus alternative layers of oxygen and Mg were formed which result in (111) orientation of the MgO film.

Fig.3 shows the SEM photographs of surface and cross-section views of MgO thin films. (100) and (111) oriented films had columnar structure. Columnar size of (100) and (111) oriented films was estimated from SEM surface micrographs to be 150-200nm and 100-130nm, respectively. Amorphous film consisted of fine grains about 50-60nm in size.

4. Conclusions

MgO films were prepared at 300 to 600℃ on Si(100) from Mg-DPM by PE-CVD. At the substrate temperature 300 and 400℃, (220) oriented MgO films were obtained at lower O_2 flow rate. The increase in O_2 flow rate , orientation of MgO films changed from (220) to (200). And amorphous MgO films were prepared at O_2 flow rate above 20 cm^3 / min. At the substrate temperatures 500 and 600℃, (111) oriented MgO films were obtained at lower O_2 flow rate, and further increase in O_2 flow rate, (220) and (200) oriented MgO films were prepared in order as increase in the O_2 flow rate. (100) and (111) oriented MgO films had a columnar structure.

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