Growth of magnesium oxide thin films using single molecular precursors by metal–organic chemical vapor deposition

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\textbf{Abstract}

Thin films of MgO have been deposited on Si(100) and c-plane sapphire substrates by the metal–organic chemical vapor deposition (MOCVD) method using Mg\textsubscript{2}(tmhd)\textsubscript{2} and Mg(acac)\textsubscript{2} as single molecular precursors and oxygen as carrier gas. We have synthesized the metal–organic precursors used in this study. Strongly [111] oriented polycrystalline MgO films were obtained on both Si(100) and c-plane sapphire substrates using these precursors in the temperature range 500–600°C. The MgO thin films grown on Si(100) at 600°C and on c-plane sapphire at 500°C with Mg(tmhd)\textsubscript{2} are highly oriented in the [111] direction, whereas the MgO film grown on Si(100) at 350°C and then annealed at 520°C has no preferred orientation. In the case of using Mg(acac)\textsubscript{2} as precursor, however, the MgO film deposited on c-plane sapphire surface at a deposition temperature above 500°C was grown with more [110] and [100] dominant orientation relatively rather than [111]. Furthermore, we have also shown that the synthesized precursors Mg(tmhd)\textsubscript{2} and Mg(acac)\textsubscript{2} are suitable precursors for obtaining MgO thin films by MOCVD and the substrate or precursor type and the growth temperature will be important factors influencing either the crystal growth direction or the crystallinity of the films. © 1999 Elsevier Science S.A. All rights reserved.

\textit{Keywords:} MgO; MOCVD; Single molecular precursors; Silicon; Sapphire

1. Introduction

Magnesium oxide (MgO) thin films have attracted much attention in the preparation of niobium nitride Josephson junctions as an underlayer, on the basis of the fact that MgO and NbN have the same crystalline structure with only a 4% difference in lattice constant. In addition, MgO films are attractive as large-area substrates or buffer layers for growing oriented high-$T_c$ superconducting thin films [1–4]. The most important point in these applications is the preparation of highly [100] oriented MgO thin films [5].

High quality MgO thin films have traditionally been prepared by spray pyrolysis [6,7], plasma-enhanced chemical vapor deposition [8], and metal–organic chemical vapor deposition (MOCVD) [9–12] techniques. MgO is a highly ionic insulating crystalline solid with the rock salt structure. It has f.c.c. Mg and O sublattices, and low energy neutral [100] cleavage planes. Its refractive index and dielectric constant are 1.74 and 10, respectively. The lattice constant of MgO is 4.21 Å, whereas those of silicon and sapphire are 5.43 Å and 5.13 Å respectively, implying a mismatch of 22.5% between MgO and Si and 19.7% between MgO and sapphire. Therefore, epitaxy of MgO films directly on silicon and sapphire is rendered difficult by several factors, including high growth temperature, interdiffusion, large lattice constant mismatch, and general lack of epitaxy to the rock salt structure. Recently Lu et al. [9] grew thin MgO films with [100] orientation on SrTiO\textsubscript{3} and c-plane sapphire substrates at temperatures below 600°C from Mg(tmhd)\textsubscript{2} by MOCVD. But when the temperature was higher than 600°C, films with both [100] and [111] orientations were grown. Boo et al. [10] deposited highly [100] oriented polycrystalline MgO films on GaAs(100) substrates at substrate temperatures as low as 350°C using Mg(tmhd)\textsubscript{2} by MOCVD. Kwak et al. also used Mg(tmhd)\textsubscript{2} as precursor and argon as carrier gas [11]. They deposited highly [100] oriented polycrystalline MgO films on fused quartz substrates at 740°C and poorly polycrystalline MgO films on Si(100) above 650°C by thermal CVD. Murayama and Shionoya [12] used magnesium 2-ethylhexanoate and prepared polycrystalline MgO films on amorphous substrates at 440°C by low-temperature atmospheric-pressure CVD. However, they only grew poorly crystalline films on Si(100) at 550°C. DeSisto and Henry made MgO films on Si(100) and sapphire by spray pyrolysis of an aqueous magnesium acetylacetonate solution [6,7]. The MgO films on Si(100) and sapphire showed no crystallinity as depos-

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ated at 400 and 550°C, but for the MgO films on sapphire, [100] orientation occurred after annealing at 700 and 930°C.

To our best knowledge, however, no epitaxial MgO films on Si(100) and c-plane sapphire substrates have been reported yet. In this paper, therefore, we report here preliminary results on the growth of MgO thin films on silicon and sapphire substrates. We used Mg(tmhd)$_2$ and Mg(acac)$_2$ as single molecular precursors and prepared highly crystalline MgO films on Si(100) and c-plane sapphire at substrate temperatures between 350 and 600°C. The low temperature conditions employed in this study enabled us to deposit thin films of MgO on Si(100) and c-plane sapphire without appreciable cracking and interdiffusion.

2. Experimental

Mg(tmhd)$_2$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate anion) and Mg(acac)$_2$ (acac = 2,4-pentanedionate or acetylacetonate anion) were used as single molecular precursors. Mg(tmhd)$_2$ was prepared by the reaction of Mg powder (Kanto Chemical Co., Inc.) with Htmhd (Strem Chemicals Inc.) in methanol. It was identified by proton nuclear magnetic resonance spectroscopy ($^1$H NMR), Fourier transform IR spectroscopy (FT-IR), thermogravimetric analysis and differential thermal analysis (TGA and DTA), and mass spectrometry. Mg(acac)$_2$ was also synthesized by a well known method [13,14]. In both cases the Mg(tmhd)$_2$ and Mg(acac)$_2$ were recrystallized from THF (tetrahydrofuran) and methanol, respectively, and then dried under vacuum.

Thin films of MgO were prepared using a CVD apparatus. Si(100) wafer and c-plane sapphire were used as substrates. The substrates were cleaned, just prior to deposition, with trichloroethylene, followed by rinsing with acetone, deionized water, and methanol. The Si substrate was then treated with 20% HF and 36% HCl solutions, to remove the surface oxide layer. Details of the experimental set-up and process have already been reported elsewhere [10,15]. The general condition of deposition pressures, temperatures, and time for MgO thin film growth on Si(100) and c-plane sapphire substrates were 10–30 mTorr, 350–600°C, and 2 h, respectively. The substrate temperature was monitored by a chromel–alumel thermocouple placed on the top of the substrate. Oxygen was used as carrier gas with a flow rate in the range 10–50 sccm.

The composition of the MgO thin films was determined by X-ray photoelectron spectroscopy (XPS). The crystallinity of the films was analyzed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

![Fig. 1. X-ray diffraction pattern and SEM image of the MgO thin film deposited on Si(100) using Mg(tmhd)$_2$ as precursor at 600°C: (a) XRD, (b) SEM.](image)

![Fig. 2. X-ray photoelectron survey spectrum and high resolution XP spectra of the MgO thin film deposited on Si(100) using Mg(tmhd)$_2$ as precursor at 600°C: XP survey spectrum (a) and high resolution XP spectra of Mg(1s) (b) and O(1s) (c).](image)
3. Results and discussion

3.1. MgO on Si(100)

The MgO films were grown on Si(100) substrates at temperatures between 350 and 600°C. Fig. 1a shows the X-ray diffraction pattern of an MgO thin film on Si(100) using Mg(tmhd)_2 as precursor at 600°C. The XRD pattern of the as-grown MgO thin film shows two dominant peaks at 2θ = 36.8° and 78.6° attributed to the (111) and the (222) planes of cubic-type MgO crystal, indicating that the film is predominantly textured with [111] orientation. The other peaks appeared at 2θ = 32.6°, 61.0°, and 69.1° were attributed to the silicon substrate. A SEM photograph of a typical MgO film grown on Si(100) at 600°C from Mg(tmhd)_2 is shown in Fig. 1b, revealing a good crystalline surface with small grains predominantly grown with [111] orientation. From the results of XRD and SEM, therefore, we conclude that the MgO thin film grown on Si(100) surface at 600°C is highly [111] oriented and the synthesized Mg(tmhd)_2 can be a suitable precursor for obtaining MgO thin film by MOCVD. Quite similar results were obtained on Si(100) substrates at 550°C, but the crystallinity of the film is somewhat poorer than that observed at 600°C.

In the case of using Mg(acac)_2 as precursor, a similar result was also obtained by the MgO film grown on Si(100) at 550°C under the same deposition condition, indicating the same relationship between crystal growth direction and growth temperature (or crystallinity). Judging from the relative XRD peak intensity ratio of (110)/(111) and (100)/(111), however, the MgO film on Si(100) grown at 550°C with Mg(acac)_2 has more [110] or [100] preferred orientation relatively rather than [111] which was obtained by MgO film grown at 600°C with Mg(tmhd)_2. This suggests that the precursor type can be influenced with a dependence on the crystal growth orientation.

Fig. 2a shows an X-ray photoelectron survey spectrum of the MgO thin film deposited on c-plane sapphire using Mg(tmhd)_2 as precursor at 500°C: (a) XRD, (b) SEM.

In Fig. 2a, the photoelectron peaks of Mg(1s), Mg(2s), Mg(2p), and O(1s) are seen together with the C(1s) peak. This C(1s) peak invariably shows up on all of the XP spectra (even with clean MgO single crystals) and can be attributed to surface contamination of the film and/or carbon incorporation into the film. Depth profiling of the film has not been attempted at the moment. From Mg(1s) and O(1s) XP high resolution peaks (Figs. 2b,c), however, we know that the stoichiometry of the as-grown MgO thin film is correct, indicating 1:1 ratio of magnesium to oxygen.
It is the same as that obtained with a clean MgO single crystal within the experimental errors of XPS. Moreover, this result is also very similar to those obtained with other silicon substrates and c-plane sapphire substrates.

Fig. 3a shows the X-ray diffraction pattern of MgO thin film deposited on Si(100) surface at 350 °C using Mg(tmhd)2 as precursor and then annealed at 520 °C using oxygen as carrier gas. In Fig. 3a, four major XRD peaks attributed to (111), (200), (222), and (400) of MgO appear at 2θ = 36.8°, 42.8°, 78.6°, and 90.9°, respectively, indicating that the film is polycrystalline with no dominant orientation. Comparing the increase in the intensity ratio of (100)/(111) XRD peaks with Fig. 1a, however, it is evident that the MgO thin film on Si(100) substrate deposited at 350 °C and then annealed at 520 °C has more [100] preferred orientation than that deposited at 600 °C, showing a direct dependence of growth temperature on the film growth direction and/or the crystallinity. This is in good agreement with results reported previously [6,7]. DeSisto and Henry made MgO films on Si(100) and sapphire substrates at 400 and 550 °C by spray pyrolysis of an aqueous Mg(acac)2 solution and showed no crystallinity. For the MgO films on sapphire, however, [100] orientation occurred after annealing at 700 or 930 °C. The morphology of this MgO film is shown in Fig. 3b. The MgO film surface consists of cubic and triangular pyramidal particles mainly grown normal to the substrate surface, signifying [111] orientation. But, some of the MgO crystals are shown to grow along the [100] direction. This is in good agreement with the XRD result.

3.2. MgO on c-plane sapphire

The MgO films on c-plane sapphire surfaces were grown at temperatures between 500 and 600 °C. Fig. 4a shows the X-ray diffraction pattern of an MgO thin film grown on c-plane sapphire at 500 °C using Mg(tmhd)2 as precursor. In Fig. 4a, the XRD pattern shows strong (111) and (222) peaks, and weak (220) and (200) peaks. This indicates that the MgO film has highly [111]-oriented crystals. The surface morphology of the same MgO film is shown in Fig. 4b with a magnification of 30,000. There exist some faceted hillocks and pits, but Fig. 4b does not exhibit any features that can be clearly attributed to cracks and pinholes.

Fig. 5a shows the X-ray diffraction pattern of MgO thin film deposited on c-plane sapphire substrate at 550 °C using Mg(tmhd)2 as precursor. Comparing Fig. 5a with Fig. 4a, the XRD pattern of Fig. 5a is more complicated. Taking into account the intensity of the (111) reflection is 11% of that of...
the (200) reflection, however, the (111) and (222) peaks due to the [111] oriented film grown at 550°C are still highly pronounced even though the (200) XRD peak shows strongly as a major peak. Judging by the relative peak heights (i.e. intensity ratio of (100)/(111) XRD peaks), however, the portion of (100) peak was increased, signifying a change of preferred crystal growth orientation. This means that the MgO film grown at 550°C has much higher [100] orientation relative to than that grown at 600°C, suggesting a reverse trend between the Si(100) and the c-plane sapphire substrate. This is a very similar result to that reported by Lu et al. [9]. They grew thin MgO films with [100] orientation on SrTiO3 and r-plane sapphire at temperatures below 600°C from Mg(tmhd)2 by MOCVD. But when the growth temperature was higher than 600°C, films with both [100] and [111] orientations were grown showing a temperature dependence on the growth direction and the crystallinity. Therefore, this implies that the substrate or precursor together with growth temperature will be one of the important factors determining the crystal growth direction and crystallinity. A SEM photograph of the MgO thin film grown on c-plane sapphire at 550°C is shown in Fig. 6a, revealing a cubic crystalline surface with small-sized crystallites.

The X-ray diffraction pattern of an MgO thin film deposited on c-plane sapphire substrate using Mg(acac)2 at 600°C is shown in Fig. 5b, indicating that the as-grown MgO film has crystallinity. This is very similar to the result of the MgO film obtained at 550°C using the precursor Mg(tmhd)2 as shown in Fig. 5a. Moreover, the morphology shown in Fig. 6b is also quite similar to the MgO film (Fig. 6a) deposited on c-plane sapphire at 550°C using Mg(tmhd)2. Comparing the variation of the relative intensity ratios (i.e. (200)/(111) and (220)/(111)) in Fig. 5a and Fig. 5b, we can expect that the precursor Mg(tmhd)2 may be a more suitable MO source than Mg(acac)2 for growing epitaxial MgO film. In this study, however, it is still not clear yet whether the precursor type can influence the crystal growth orientation or not. A better understanding and further experiments on the deposition process controlling epitaxial growth of single-crystal MgO thin films on Si(100) and c-plane sapphire substrates are still necessary.

4. Conclusions

We have deposited crack-free thin, uniform, and stoichiometric films of MgO on Si(100) and c-plane sapphire surfaces by a single source MOCVD technique using Mg(tmhd)2 and Mg(acac)2 as the metal–organic single molecular precursors. Highly [111] oriented polycrystalline MgO films were obtained on Si(100) and c-plane sapphire substrates using these precursors at temperatures between 500 and 600°C. However, in the case of the MgO film grown on Si(100) at 350°C and then annealed at 520°C with Mg(tmhd)2, polycrystalline films with no preferred orientation were obtained. At temperatures above 600°C, moreover, polycrystalline films with more [110] and [100] preferred orientation relatively rather than [111] could also be deposited on c-plane sapphire from both precursors. Furthermore, we have also shown that Mg(tmhd)2 and Mg(acac)2 are suitable precursors for obtaining MgO thin films by the low temperature MOCVD technique and the substrate or precursor type and the film growth temperature can be important factors influencing the crystal growth direction and crystallinity.

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