Articles

Atmospheric Pressure Atomic Layer Epitaxy of ZnO Using a Chloride Source

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Received August 16, 2000. Revised Manuscript Received April 10, 2001

We examined the epitaxial growth of ZnO films on a sapphire (0001) substrate by an atmospheric pressure atomic layer epitaxy technique using $ZnCl_2$ and O_2 sources. The films were deposited epitaxially in a substrate temperature range of 450−550 °C with a constant growth rate of 0.26 nm/cycle. It is noteworthy that the rate corresponds to just a half-length of the *c* axis of hexagonal ZnO, indicating that the alternate deposition of $ZnCl_2$ and O_2 on the substrate is governed by a self-limiting mechanism. This was also confirmed by the facts that the film thickness was dependent only on the growth cycles and that the surface was quite smooth. A strong photoluminescence band edge emission of 3.36 eV was observed at 20 K.

Introduction

Artificial construction of atomically defined metal oxide layers is important in making electronic devices including light-emitting materials, high-temperature superconducting oxide films, and magnetic devices as well as other advanced materials. Hence, an understanding of the epitaxial growth process on metal oxide surfaces at the atomic level is required in order to fabricate atomically controlled structures that exhibit unexplored and interesting physical properties.

Atomic layer epitaxy (ALE) is the most promising growth technique for fabricating these structures and for understanding these growth processes, because this method can control growth monotonically by a self-limiting mechanism. So far, ALE has been applied to the growth of some binary compound semiconductors using metal−organic vapor-phase epitaxy (MOVPE), metal−organic molecular beam epitaxy (MOMBE), and hydride vapor-phase epitaxy (VPE) systems.[1] In recent years, control of the growth of metal oxide films by means of ALE has also become necessary at the atomic level.

ALE has been employed in ZnO film growth on glass and plastic substrates. Commonly used zinc and oxygen sources include acetate[2] and metal−organic compounds,[3] and water in the ALE depositions, respectively. However, strong research for epitaxial films has not been performed because of the interest devoted to transparent conducting layers grown under low pressure.

We examined the epitaxial growth of ZnO films on a sapphire (0001) substrate by means of the atmospheric pressure ALE (AP-ALE) technique using $ZnCl_2$ and O_2 as starting materials. The advantage of AP-ALE is that the formation of oxygen defects is significantly suppressed, allowing the creation of complicated stoichiometric oxide films. In addition, the crystal structure, surface morphology, and optical properties of the ZnO were also investigated.

Experimental Section

AP-ALE growth was carried out in a horizontal-type quartz hot-wall reactor which was designed for this study. The apparatus used is illustrated in Figure 1. Each source material and purge gas was introduced independently into the reactor. $ZnCl_2$ was evaporated at a temperature of 400 °C, being provided into the growth zone using purified N_2 as a carrier gas. O_2 was diluted with purified N_2. To prevent $ZnCl_2$ and O_2

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10.1021/cm0006594 CCC: $20.00

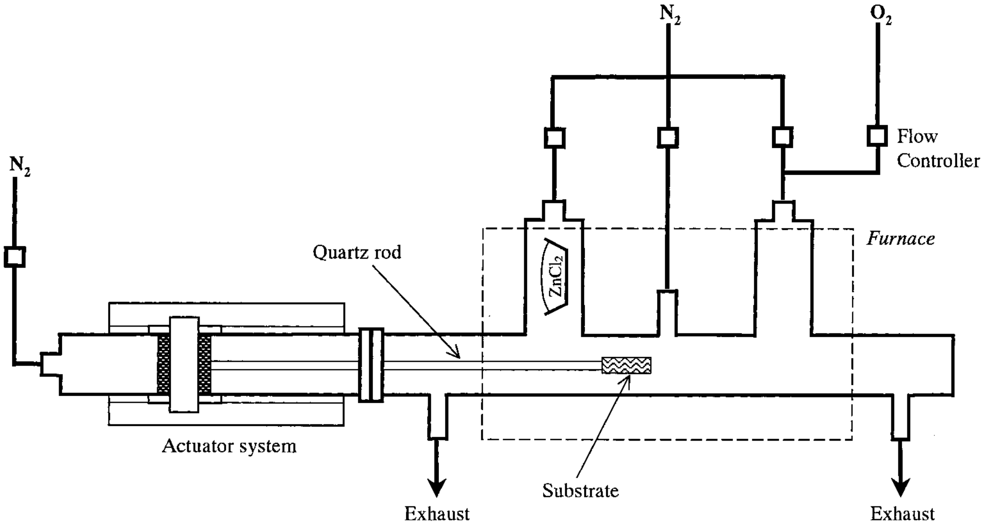

Figure 1. Schematic diagram of the experimental apparatus for AP-ALE.

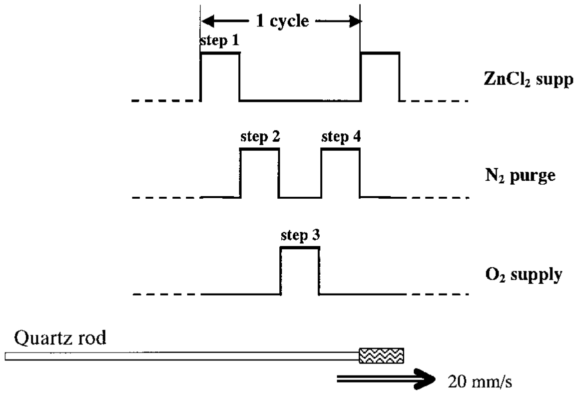

Figure 2. Gas flow sequence for AP-ALE.

Table 1. Typical Growth Conditions of ZnO Film Grown by AP-ALE

substrate	sapphire (0001)
growth temp	400–600 °C
ZnCl$_2$ partial pressures	3.50×10^{-5} to 3.50×10^{-4} atm
O$_2$ partial pressures	5.00×10^{-2} to 5.00×10^{-1} atm
exposure periods	2.5–20 s
total gas flow rate	200 sccm

from mixing with one another, they were separated by N$_2$ gas flowing in between. The substrate was mounted on a quartz rod as shown in Figure 1. ZnCl$_2$ and O$_2$ were supplied alternately to the substrate by moving the rod forward and backward with a computer-controlled actuator system as indicated in Figure 2. The sequence of a single deposition cycle has four steps as follows: ZnCl$_2$ supply (step 1), N$_2$ purge (step 2), O$_2$ supply (step 3), and N$_2$ purge (step 4). This cycle was repeated 50–1200 times/run. The details of the growth conditions are listed in Table 1.

All substrates were optical-grade polished sapphire (10 × 10 mm) with (0001) orientation (*c* face). The roughness and the misorientation were within 0.4 nm and ±0.5°, respectively. The sapphire was degreased by successive cleanings in acetone and deionized water and chemically etched with a hot solution (160 °C) of H_3PO_4–H_2SO_4 (1:3) for 10 min before being dried in a stream of dry nitrogen. High-purity zinc chloride (99.999% ZnCl$_2$) and high-purity oxygen gas (99.995% O$_2$) were used as the Zn and O sources, respectively.

The film thicknesses of the ZnO films were determined by means of a profilometer by surface roughness measurement (Rank Telar Bobson Co.). The crystallinity and surface morphology were examined by double-crystal X-ray diffraction analyses (Rigaku Co., RINT 2000 X-ray diffractometer) and atomic force microscopy (AFM; Shimadzu Co., SPM-9500), respectively. Photoluminescence (PL) measurements were carried out by exciting the samples with light of 325 nm (He–Cd, 15 mW).

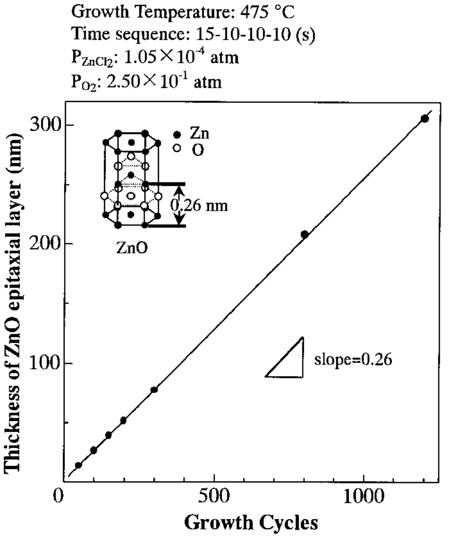

Figure 3. Relationship between the ZnO film thickness and the growth cycle at 475 °C.

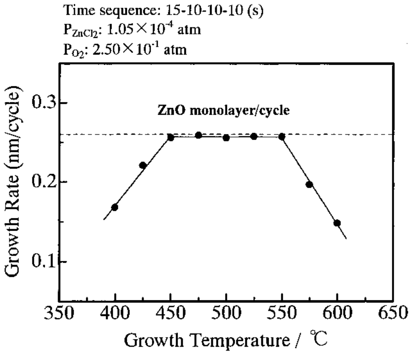

Figure 4. Growth rate of the ZnO films as a function of the growth temperature.

Results and Discussion

Figure 3 shows the relationship between the ZnO film thickness and the growth cycle at 475 °C. The film

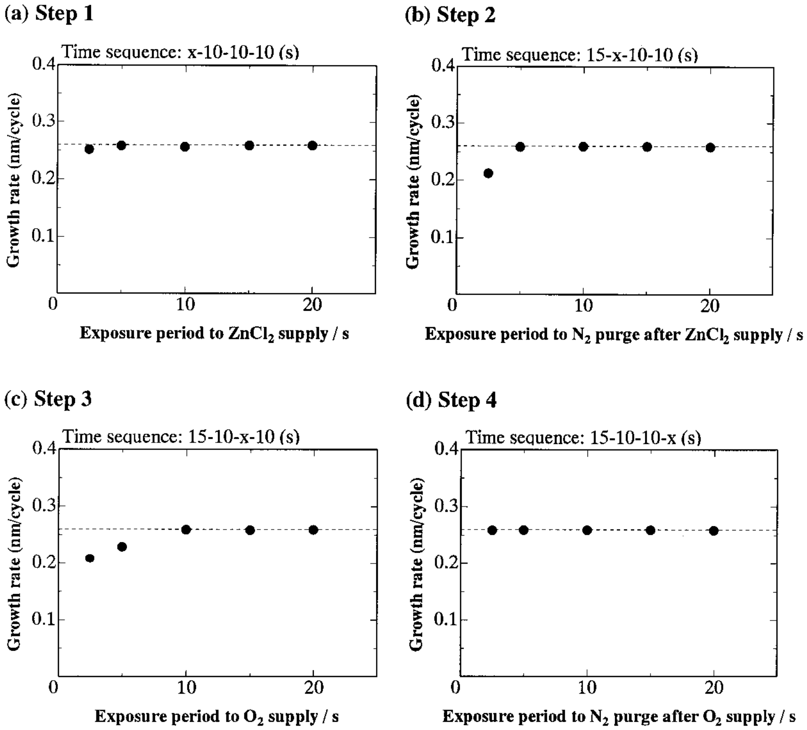

Figure 5. Growth rate as a function of the exposure period to (a) $ZnCl_2$ supply, (b) N_2 purge, (c) O_2 supply, and (d) N_2 purge, respectively. The $ZnCl_2$ and O_2 partial pressures were kept constant at 1.05×10^{-4} and 2.50×10^{-1} atm, respectively.

thickness increases linearly with the growth cycle over the whole range examined in the study. The slope of a straight line shown in Figure 3 is 0.256 nm/cycle. It is noteworthy that the served growth rate is close to half of the lattice parameter c (0.520 661 nm) of the bulk ZnO crystal with hexagonal symmetry.[4] As can be seen from the crystal structure of the hexagonal ZnO in Figure 3, this means that a single cycle growth corresponds to the distance between adjacent Zn layers. Additionally, no film thickness change can be observed without O_2 supplies. This provides evidence of Langmuir adsorption in which a saturated adsorbate layer is obtained during a single $ZnCl_2$ supply. Consequently, it is confirmed that the alternate deposition of $ZnCl_2$ and O_2 on the sapphire substrate is governed by a self-limiting mechanism.

Figure 4 shows the growth rate of the ZnO films as a function of growth temperature. The rate was estimated from the films of 200 cycles, and the dashed line denotes $c/2$ of the bulk ZnO crystal. It is seen that the growth rate increases with increases in temperature and reaches a plateau of 0.257 nm/cycle at 450 °C. In the present study, the distinct ALE window where the growth rate is independent of the temperature is observed in the temperature range of 450−550 °C. Further increase in the temperature above 550 °C decreases the growth rate because of the desorption of $ZnCl_2$ and O_2 from the substrate surface.

Figure 5 shows the growth rate as a function of the exposure period to $ZnCl_2$ and O_2 supplies and N_2 purges, respectively. Each exposure period was changed in the range of 2.5−20 s. As in Figure 4a, the growth rate for the $ZnCl_2$ supply period is almost 1 monolayer/cycle under a wide range of exposure periods. However, the growth rate for the O_2 supply shown in Figure 4c is different from that for the $ZnCl_2$ supply and gradually decreases at an exposure period of less than 5 s. It is thought that this decrease of the growth rate was caused by the incomplete reaction between the substrate surface and oxygen in the ZnO formation. In Figure 4b,d, the growth rates are independent of the N_2 purge period except for that after $ZnCl_2$ supplied for less than 2.5 s. The reason the growth rate decreases for a short N_2 purge period after the $ZnCl_2$ is supplied is not clarified.

Figure 6 shows the growth rate as a function of the $ZnCl_2$ and O_2 partial pressures, respectively. As can been seen from Figure 5a, the monolayer growth per cycle with a self-limiting deposition was obtained in all of the $ZnCl_2$ partial pressures examined. However, for the O_2 supply in Figure 5b, the growth rate was less than 1 monolayer at partial pressures of lower than 1.00×10^{-1} atm. Therefore, it is found that a rather high O_2 partial pressure compared with the $ZnCl_2$ partial pressure is required for the complete reaction with O_2.

Metal chlorides have been applied as a metal source in ALE growth of the corresponding oxide films.[5] However, these metals seem to suffer from a low reactivity with oxygen. For example, though $TaCl_5$ and O_2 sources have been used for ALE growth of tantalum oxide under low pressure, it is difficult to produce a high growth rate of tantalum oxide deposition without photoexcitation.[6] In comparison with the ALE growth under low pressure, our AP-ALE technique allows the use of O_2 at high partial pressure, which allows a complete oxygen reaction to take place during the ALE growth. As a consequence of these features, it is thought that the ZnO films were successfully grown by alternate

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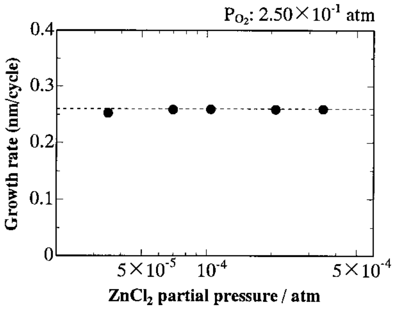
(a) Step 1



(b) Step 3

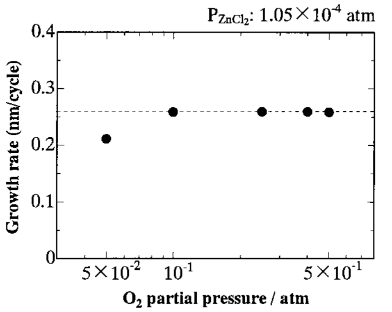


Figure 6. Growth rate as a function of (a) $ZnCl_2$ and (b) O_2 partial pressures, respectively. The exposure period to each gas was as follows: $ZnCl_2$ supply for 15 s, N_2 purge for 10 s, O_2 supply for 10 s, and N_2 purge for 10 s.

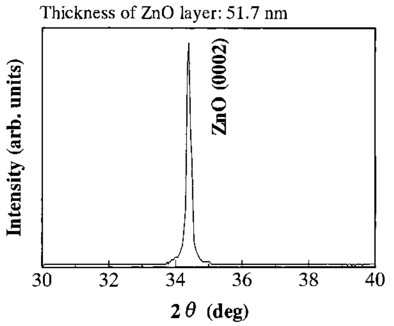
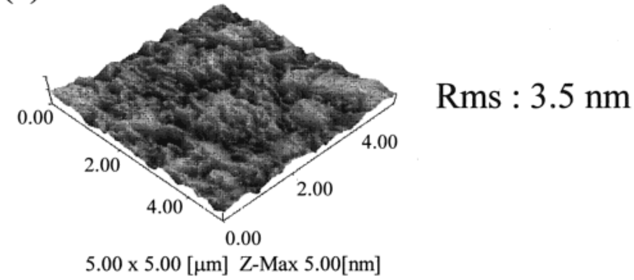


Figure 7. Representative double-crystal X-ray diffraction pattern of the ZnO film for 200 cycle growth at 475 °C. The film thickness was 51.7 nm.

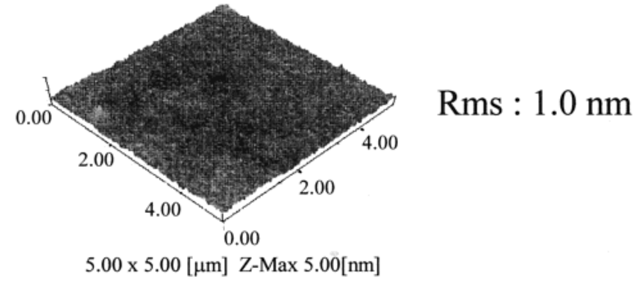
reactions of $ZnCl_2$ and O_2. In the ZnS growth, the calculations made by Pakkanen et al.[7] showed that the maximum growth rate can be $^1/_2$ of the ideal, and if the $ZnCl_2$ molecules orient differently, the rate is $^1/_3$ of the ideal. This is because of the large size of chloride ions. The reason the $ZnCl_2$ adsorption is saturative at the surface in the ZnO formation is not clarified. However, it would be clarified by the further investigations of the growth mechanism utilized for the self-limiting growth process in $ZnCl_2$ and O_2 molecules.

Figure 7 shows a representative double-crystal X-ray diffraction (DC-XRD) pattern of the ZnO film grown at 200 cycles at 475 °C. An intense diffraction peak appearing at 34.4° is assigned to the (0002) reflection of the hexagonal ZnO, implying that the ZnO film has a *c*-axis orientation normal to the sapphire (0001) plane. In other words, this suggests that the ZnO film is epitaxially grown on the substrate. The full width at half-maximum (fwhm) of the (0002) diffraction was 9.3 min. Similar results were obtained for all samples. Usually the ZnO films grown by ALE are amorphous or polycrystalline on glass and plastic substrates. As a result, ZnO films with a single orientation can be obtained by means of a *c*-sapphire substrate.

(a) 400 °C



(b) 475 °C



(c) 600 °C

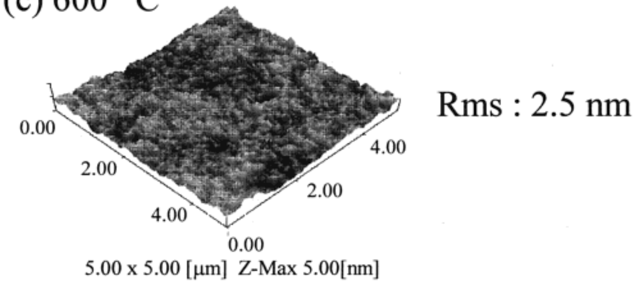


Figure 8. AFM images of the ZnO film for 200-cycle growth. The growth temperatures are (a) 400, (b) 475, and (c) 600 °C.

Figure 8 shows the AFM images of a ZnO surface obtained at various growth temperatures. The film thickness was 200 monolayers for all samples. As is clearly evident from the AFM images, a much more smooth surface with less than 1.0 nm of the mean-square roughness (rms) was obtained at a growth temperature of 475 °C, while very rough surfaces were observed at temperatures of 400 and 600 °C. The results of Figures 4 and 8 show how the growth rate affects the film roughness. For the films grown at temperatures of 400 and 600 °C, ZnO coverage is partly given on the original substrate at the first cycle because of the adsorption of less than 1 monolayer, and then the ZnO overlayer is adsorbed on 1 cycle growth with the ZnO step. As a result, it is thought that the rough surfaces were caused by repeated formations of the ZnO step because of the growth rate of less than 1 monolayer.

Figure 9 shows the PL spectrum of the ZnO film grown at 200 cycles at 475 °C, which was measured at 20 K. A strong peak centers at approximately 3.36 eV, corresponding to the band edge emission of the ZnO.

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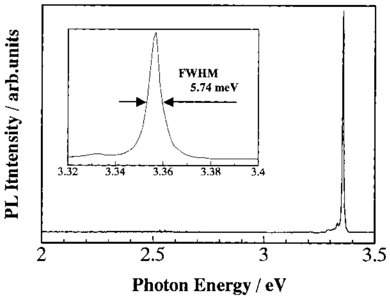

Figure 9. PL spectrum at 20 K of the ZnO film for 200-cycle growth at 475 °C.

The fwhm of the band edge peak was 5.74 meV. Many reports have suggested that green−yellow photoluminescence emitted from ZnO powders and polycrystals is due to some point defects (luminescent centers) such as oxygen and zinc vacancies in the crystals. However, no emission peak is observed in the visible region because of the deep-level impurities and/or lattice defects. Also, it is confirmed by XPS analysis that the chlorine percentage in the film is below 1 atom % of the identification limit. Therefore, it is concluded that the high-quality ZnO film of the stoichiometry was formed in the present study.

Conclusions

ZnO films were successfully grown on sapphire (0001) substrates by means of the AP-ALE technique utilizing the alternate reaction of $ZnCl_2$ and O_2. Epitaxial ZnO films were obtained at 450−550 °C. The growth rate was about 0.26 nm/cycle corresponding to a ZnO monolayer/cycle, which indicates that the ZnO films were formed by the self-limiting mechanism. A smooth surface with less than 1.0 nm of rms was obtained in the ALE window. The saturated reaction of ALE was achieved at a sufficient exposure period and high O_2 partial pressure. As a result, the PL spectrum at 20 K exhibited a strong peak at about 3.36 eV, corresponding to the band edge emission.

Acknowledgment. This work was partly supported by the Sasakawa Scientific Research Grant from The Japan Science Society, by the Izumi Science & Technology Foundation, and by the Japan Society for the Promotion of Science through a grant-in-aid for scientific research (A) No. 12355030.

CM0006594