Highly Oriented ZnO Films Prepared by MOCVD from Diethylzinc and Alcohols

S. Oda, H. Tokunaga, N. Kitajima, J. Hanna, I. Shimizu and H. Kokado

Imaging Sci. & Eng. Lab., Tokyo Institute of Technology

Nagatsuda, Midori-ku, Yokohama 227, Japan

Alcohols are shown to be useful as oxidizing agents of diethylzinc for the growth of ZnO films by MOCVD. C-axis oriented ZnO films have been produced on glass substrates at around 300°C. The problem of premature reaction which is observed between diethylzinc and oxygen or water vapor, is shown to be overcome when alcohols are used in their stead. The formation, stability and decomposition of the precursor of MOCVD, adducts, are discussed on the basis of mass spectroscopy analysis.

1. Introduction

It has been reported that c-axis oriented ZnO films can be deposited on a wide variety of substrate materials, including supphire and glasses, at fairly low temperatures by $\text{sputtering}^{(1)}$ or by $\text{CVD}^{(2)}$. Such oriented films can be applied to optical or photoelectric imaging devices if it is established the method to control the properties of ZnO films and to grow films at a practical rate.

Several authors have reported the MOCVD of $\text{ZnO}^{3)-6}$. Diethylzinc(DEZ) or dimethylzinc(DMZ) are oxidized by 0_2 , H_20 , CO_2 or N_20 . These oxidizing agents, however, have not given quite satisfactory results. On one hand, it is difficult to control the deposition of ZnO by using DEZ and either 0_2 or H_20 because they react prematurely upstream from the substrate, resulting in the formation of white powder. If CO_2 or N_20 , on the other hand, are used as oxidizing agents, it takes long time to grow films because of slow reaction.

Some attempts have been made to overcome these problems; e.g., by using a low pressure in the reactor chamber and by mixing the gases very near the substrate surface to prevent the premature reaction. Shiosaki et al⁶ obtained a uniform film of c-axis oriented ZnO on a glass substrate at 200°C by employing rf plasma in DEZ and CO₂ system. For the growth of Ill-V compounds by MOCVD adducts, such as $(CH_3)_3 InP(C_2H_5)_3$, has been used successfully. Recently, Wright et al.⁷⁾ used heterocyclic compounds, instead of group VI hydrides, in reaction with DMZ to produce ZnS, ZnSe and ZnO films. Sritharan and Jones⁸⁾ mixed DMZ and diethylselenide to form a $(CH_3)_2 ZnSe(C_2H_5)_2$ adduct to prevent the room temperature reaction between DMZ and H₂Se.

This paper deals with a new approach to the problem of premature reactions in the MOCVD process of ZnO films employing alcohols(R-OH) as oxidizing agents for DEZ. DEZ and R-OH may react easily to form zincalcoholate, R-OZnO-R, which can be transported to the deposition zone. Otherwise they may form the adducts, $(C_2H_5)_2$ ZnORH. As both the reactivity of R-OH with DEZ and the stability of the precursor depend upon the length and the form of alkyls, it may be possible to obtain a suitable precursor by choosing R-OH.

2. Experimental

The apparatus used for the MOCVD of ZnO films is schematically illustrated in Fig. 1. The substrates were heated by a built-in resistor. The reaction chamber geometry was horizontal with gas flow at an angle of 15° to the substrate surface. The chamber was a quartz tube with a 50cm long, 5cm diam at the ends, 10cm diam at the central deposition zone. The pressure of the reactor tube was adjusted between $8-40 \times 10^3$ Pa by employing a rotary pump and a throttling valve. Both DEZ and R-OH were contained in stainless steel bubblers immersed in a temperature controlled bath, usually kept at 25°C. The amount of DEZ and R-OH transported to the reactor was set to 5.4×10^{-5} mol/min and $1.3-9.0 \times 10^{-3}$ mol/min, respectively, by control-



Fig. 1 Schematic diagram of ZnO deposition system.

ling the flow rate of He carrier gas. Surviving chemical species in the exhaust gas were monitored by a quadrapole mass filter using a differential pumping system which consists of a turbo-molecular pump, a diffusion pump, an orifice and a gate valve.

3. Results and discussion

Figure 2 shows the growth rate as a function of substrate temperature for three alcohols and water, while mainting all other growth parameters constant as shown in the figure. At low temperatures for alcohols the growth rate increases as the growth temperature is increased. The decomposition of precursors are thermally activated. At high temperatures the growth rate drops due to the reactant depletion at the substrate surface. Depositions of white powder was observed at the inner surface of the reactor tube instead. Therefore, the position of the peak in the growth rate shown in Fig. 2 will change with different size and design of reactor tube geometry. When H₂O is used as an oxidizing agent the growth rate decreases as temperature is raised even at low temperature regions. In this case the precursor, Zn(OH)2, is not stable above 125°C. In addition, the vapor pressure of Zn(OH) 2 is lower than zincalcoholate. Hence, it is more likely to introduce nucleation growth, resulting in opaque film with large number of light scattering centers. Therefore it is difficult to control the growth of ZnO by employing H₂O as an oxidizing agent.

However, it has been found that small amount of water incorporated in alcohols plays still an important role in the growth of ZnO films. At the first stage of our work properties of the films considerably scattered. Then alcohols were purified thoroughly and water was added carefully. ZnO films were tend to be peeled off easily from the substrate when they were made from very pure alcohols with less than 10^{-4} mole fraction of water. With a small amount of water added to alcohols ZnO films stuck strongly to the substrates. Furthermore, the most transparent films were obtained with water content of 10^{-3} mole with respect to alcohols. Some attempts were made to clarify the role of water incorporated in alcohols in the growth of ZnO films. Deposition rates did not change significantly as water concentration varied by a factor of 500. When water was supplied at the first step of deposition and then continued to grow without water, the obtained film had the same



Fig. 2 ZnO film growth rate as a function of substrate temperature for various oxidizing agents of DEZ.



Fig. 3 Inverse of half width of (002) diffraction peak of ZnO film as a function of substrate temperature for various oxidizing agents.



Fig. 4 Dependence of RHEED pattern on thickness of ZnO films for various oxidizing agents.

properties as deposited by entirely without water. This result shows that the role of water is not limited to the nucleation process at the glass substrate but may be accounted as some catalytic action during dissociation or deposition process.

From x-ray diffraction data only (002) peak is observed in the MOCVD ZnO films. This result suggests that the c-axis of the ZnO film is oriented normal to the substrate. Fig. 3 shows the inverse of full width at half value of (002) diffraction peak plotted as a function of substrate temperature for various alcohols and water employed as oxidizing agents for DEZ. Among alcohols, tert-butanol gave rise to a crystalline ZnO film at lowest temperature, i.e., around 200°C; ethanol at 250°C. Methanol, however, did not provide any crystalline film at temperature range between 200 to 400°C. In case water was used as an oxidizing agent, a sharp (002) diffraction peak was observed at 300°C. In order to evaluate the degree of caxis orientation, rocking curves were measured at (002) peak. Standard deviation angle was smallest for ZnO film made from t-butanol compared to those made from H20 and ethanol.

Figure 4 shows the thickness dependence of the RHEED pattern of ZnO films deposited by MOCVD at 300°C. The results for three oxidizing agents were compared. Ring patterns are observed in the ZnO film made by water, while discreat spots dominate the RHEED pattern for alcohols. Tert-butanol provides the highest c-axis orientation among oxidizing agents investigated. The diffuseness of the spot decreases as the thickness of the ZnO films increases. The similar behavior of the thickness dependence of c-axis orientation in sputtered ZnO films was reported by Miura⁹⁾.

Figure 5 shows an SEM photograph of ZnO film (thickness of 7µm) grown by MOCVD with DEZ and tbutanol on a glass substrate at 300°C. An observed columnar structure normal to the substrate may be due to the c-axis orientation of the film.

Electrical conductivity of ZnO films prepared by DEZ/t-BuOH system at 300°C is 1 S/cm and its



Fig. 5 SEM photograph of ZnO film prepared by MOCVD from DEZ/t-BuOH on a glass at 300 $^\circ\text{C}$.

DEZ-tBuOH



m/e

Fig. 6 Mass spectra of DEZ/t-BuOH system for various temperatures.

activation energy is 22meV, which may be accounted for a degenerate donor level due to oxygen vacancy. Conductivity decreases as growth temperature decreases; e.g., 10^{-3} S/cm were obtained for ZnO deposited at 150°C.

A typical mass spectra for DEZ/t-BuOH system are shown in Fig. 6, taken with various heater temperatures. Zinc related peaks are easily distinguished from others because of the characteristic shape due to isotopic ratio(⁶⁴Zn:⁶⁶Zn:⁶⁸Zn= 49:28:19). Several Zn related peaks are observed in m/e of between 60 to 225. Although it is not found the peak for zinc-alcoholate (for t-butanol, m/e=210), it can not be ruled out the presence of zinc-alcoholate because some molecules may decomposed into smaller mass fragments by ionization. However, it is more likely that some adducts give rise to fragment peaks around m/e of 219 and 190 and also for smaller mass peaks. The adduct may be formed when DEZ and t-butanol meet together at room temperature. The adduct is thermally stable below 250°C and decomposes at 300°C rapidly. The temperature dependence of mass spectra of DEZ/EtOH system revealed that the adduct decomposes between 150-200°C. In case of DEZ/H20 system, the reactant may be Zn(OH) 2 which has a decomposition temperature of 125°C. The stability of the adduct or the precursor for CVD may determine the crystallographic characteristics of deposited films, because stable adducts can be transported to substrate effectively and then decomposes heterogeniously. Among oxidizing agents investigated in the present work, tert-butanol provided the best adduct properties to control the CVD process; i.e., it canbe formed adduct easily, stable below 250°C, and decomposed at around 300°C. An advantage of t-BuOH may come from its form of alkyl; not one-dimentonal chain structure but with three-dimentional spherical structure which may be effective to protect zinc atoms from the attack of foreign molecules during transpotation. This concept of the properties of precursor is also important and should be expanded into other MOCVD systems.

4. Conclusions

1) Highly c-axis oriented ZnO films have been prepared on glass substrates at around 300°C by MOCVD employing DEZ and alcohols.

2) The problem of premature reaction, which often occurs in MOCVD of ZnO, has been overcome by the use of alcohols as oxidizing agents.

3) Among alcohols tert-butanol provided defectfree and highly oriented films.

4) Mass analysis of the temperature dependence of reactant gases has shown the formation, stability and decomposition of adducts, which essentially determine the MOCVD process.

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