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環境・生命工学専攻	学籍番号	069401
申請者 氏名	ANGELITO APOSTOL VELASCO	

指導 教員	金　熙濬 田中三郎 若原昭浩

論　文　要　旨　(博士)

論文題目	**Growth Mechanism and Properties of ZnO Film Prepared by MOCVD** (MOCVD を用いて作製した ZnO 膜の成長メカニズム及びその特性)

(要旨　1,200 字程度)

酸化亜鉛は広い直接バンドギャップ（3.37 eV)、大きな励起子結合エネルギー（60 meV）そして六方晶系ウルツ鉱型の結晶構造といった多くの興味深い性質を持つ半導体である。太陽電池、発光ダイオード、UV 検出器、ガスセンサー及び弾性表面波素子に用いられている。この論文は大きく分けて二部で構成されている。前半の部では、ジエチル亜鉛（$Zn(C_2H_5)_2$、DEZ）と水（H_2O）から大気圧化学気相蒸着法（APCVD 法）を用いて生成された ZnO 膜の成長メカニズムに焦点を当てている。膜成長の律速段階となるメカニズムが気相における中間生成物の変化によって決定された。温度と管内径の関数として膜成長速度を解析することで、400～600℃の温度範囲において気相拡散が律速段階であることを明らかにした。そして実験的に測定された拡散係数から Chapman-Enskog 式を用いて、成長種の実効的な分子サイズが約 0.5nm であることを明らかにした。また 650℃における成長速度は気相反応速度定数 $k_g=60s^{-1}$ の気相反応であった。700～750℃においては、膜成長の律速段階は気相拡散であり、その分子サイズは 700℃においては約 0.9nm であり、750℃においては 0.6nm まで減少した。次にマイクロトレンチを有する Si 基盤を用いて表面反応速度定数 k_s を求めた。トレンチは深さ（L)：3.5 μ m、幅（W)：1～2.5 μ m である。モデル式を成長速度にフィッティングすることで、表面反応速度定数 k_s、付着係数 η を得た。400~500℃の温度において、40～59m/s の ks が得られた。興味深いことに、ks はより高い温度においては減少した。ks は 550 及び 600℃において 22～37m/s の、700～750℃においては 9.4～15m/s の範囲であった。さらに水冷した管を反応場に導入することにより、25～700℃の温度範囲で反応中間生成物が得られた。得られた物質の熱分解特性を示差熱熱重量同時測定（DTA-TGA）及び四重極質量分析器（QMS）を用いて調査した。反応温度 400℃で得られたサンプルの DTA パターンは 2 つの吸熱ピークが、700℃においては 3 つのピークが観察された。QMS による分析では揮発性の物質として水のみが検出された。後半の部では、DEZ、トリメチルアルミニウム（$Al(CH_3)_3$、TMA）及び水からプラズマ CVD 法（PECVD 法）を用いてアルミニウム（Al）を用いてドープした ZnO 膜を生成した。Al ドーピングは結晶サイズを減少させ、また c 軸配向性を向上させることが分かった。さらにドーピングはより高い光透過率（> 90%）及びより低い電気抵抗（最小で $6.5\times10^{-4}\Omega$cm）をもたらした。電気抵抗は TMA 流量及び基盤温度に大きく依存し、H_2O 流量及び RF 電力の影響は小さかった。

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Environment and Life Engineering Department	ID	069401
Name	VELASCO ANGELITO APOSTOL	

Advisor	Kim, Hee-Joon Tanaka, Saburo Wakahara, Akihiro

Title	**Growth Mechanism and Properties of ZnO Film Prepared by MOCVD**

(800 words)

Zinc oxide (ZnO) is a semiconductor with a wide direct band gap of 3.3 eV, large exciton binding energy of 60 meV, and a hexagonal wurtzite crystal structure. It is piezoelectric, luminescent and can be made magnetic with doping. Due to its versatility, ZnO has been employed in a wide variety of fields such as electrical circuit protection, solar cells, light emitting diodes and lasers, UV detectors, gas sensors, and surface acoustic wave devices. A brief historical background is given in Chapter 1. This thesis is divided into two parts. The first part (chapters 2 to 4) focuses on the ZnO film growth mechanism from diethylzinc ($Zn(C_2H_5)_2$) and water (H_2O) vapors by atmospheric-pressure chemical vapor deposition (APCVD) method. In Chapter 2, the rate-limiting mechanism of film growth was determined along with the molecular size of the gaseous intermediate in a flow-type tubular reactor. The substrate used was the inner surface of the quartz tube with varying diameters. The deposited films have preferential c-axis orientation according to the X-ray diffraction patterns. Scanning electron microscopy (SEM) was used to measure the film thickness along the length of the tube (x), and the growth rate (G) was calculated by dividing the thickness with the deposition time. Plots of log G versus x were linear, suggesting that the growth was limited by the DEZ concentration. The dependence of the growth rate profile on the tube diameter can be used to identify the rate-limiting mechanism. Analysis of the film growth rate profiles as a function of temperature and tube diameter revealed that the growth process is limited by the gas-phase diffusion of growth species in the temperature range of 400 to 600 °C. From the experimentally measured diffusivites and by correlating with the Chapman-Enskog equation, we obtained the effective molecular size of the growth species to be about 0.5 nm. The growth rate data at 650 °C indicates that the growth rate is limited by gas phase reaction with a rate constant, k_g of 60 s^{-1}. At 700 °C to 750 °C, the film growth was gas-phase diffusion controlled. The molecular size was about 0.9 nm at 700 °C, and decreased to about 0.6 nm at 750 °C. These sizes are equivalent to clusters consisting of as many as 20 units of ZnO at 700 °C and 6 units at 750 °C. In Chapter 3, the surface reaction constants (k_s) of the growth species were determined by using a Si substrate patterned with micron-size trenches. The trench depth (L) was 3.5 um and the width (W) changed from 1 to 3 um. This method allows the determination of k_s in an APCVD reactor because within the micro-trench the growth is limited by surface reactions. Scanning electron microscopy was used to measure the film thickness within the micro-trench. Using a model equation to fit the experimental growth rate data, we were able to determine the surface reaction rate constants, k_s or the sticking coefficients, η. At temperatures from 400 to 500°C, k_s from 40 to 59 m/s was obtained. Interestingly, k_s decreased at higher temperatures. At 550 and 600 °C, k_s ranged between 22 ~ 37 m/s and at 700 to 750 °C, k_s ranged from 9.4 to 15 m/s. In Chapter 4, the reaction intermediates in reaction of DEZ with H_2O were obtained at temperatures ranging from 25 to 700 °C by using a water-cooled substrate. The thermal decomposition properties of the samples were studied using simultaneous Differential Thermal Analysis and Thermogravimetric Analysis (DTA-TGA). A Quadrupole Mass Spectrometer (QMS) was used to identify the gases evolved during thermal decomposition. Changes in the DTA-TGA pattern were observed when the reactor temperature was increased and also during ageing at room temperature. The DTA pattern of the sample obtained at the reactor temperature of 400 °C exhibited two endothermic peaks while three peaks were present at 700 °C. QMS analysis detected only water as the volatile component during thermal decomposition. Results suggest that different types of intermediates were present depending on the reactor temperature, which agrees with the results of the previous chapters. In the second part of this thesis (Chapter 5), aluminum doped ZnO films were prepared by plasma enhanced CVD (PECVD) using DEZ, TMA and H_2O vapors. Aluminum doping was found to reduce the crystallite size of the ZnO and enhance the c-axis orientation of the films. The undoped films consist of disk-like shaped crystallites with diameter as large as 200 nm and height of about 36 nm. Al-doped films have crystallite diameters in the 100 nm range and height of about 30 nm. Doped ZnO films show better optical transmittance (>90%) and lower electrical resistivity (minimum of 6.5×10^{-4} Ωcm). The aluminum content in the film was found to depend on the growth conditions. It was generally observed that for a constant TMA flowrate, conditions resulting to low growth rates favor the incorporation of Al atoms. The electrical resistivity depended largely on the TMA flowrate and substrate temperature and less on the H_2O flowrate and RF power.