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GROWTH AND CHARACTERIZATION OF EPITAXIAL  
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## ABSTRACT

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This report contains details of the research work carried out on a one-year project on the growth and characterization of ZnO and AlN piezoelectric thin films. Material growth systems are reported for ZnO using the zinc vapor reaction with  $\text{CO}_2$ ,  $\text{ZnCl}_2$  with  $\text{O}_2$ , and the latest metal-organic process. The growth of insulating ZnO has been achieved using lithium doping during film growth. Initial results are reported for a new AlN growth process that shows promise of overcoming some previous growth problems.

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## 1.0 INTRODUCTION

This final report is for a one year's effort of an on-going research effort in the growth and characterization of piezoelectric films for use in microwave acoustic devices. The program was basically a continuation of an effort that has been conducted by the PI over the last nine years under the sponsorship of, at one time or the other; JSEP, ONR, AFML, AFCRL (RADC) and most recently AFOSR. The emphasis of the program has shifted according to the demand or interest in unique epitaxial crystal thin films and substrate combinations. The initial work on  $\text{AlN}/\text{Al}_2\text{O}_3$  was prompted by the need for high velocity substrates for microwave SAW delay lines and filters.

During the last two years an increased interest in ZnO for SAW and bulk wave devices has renewed interest in the CVD of this material. Major progress was attained in the CVD of ZnO in the last year through the achievement of high resistivity films of exceptional crystalline quality.

Of major importance to devices is the ZnO film orientation in CVD where the c-axis is in the plane of the film. This configuration allows direct shear wave generation in bulk wave delay lines implying lower propagation losses at microwave frequencies. The high growth rates, ability to dope the film during growth, increased crystal perfection, and potential for wide area coverage suggest that the CVD system will compete with sputtering as a film growth technique.

The report details the recent progress made in the CVD growth of ZnO by a number of techniques. Of considerable interest is the lower temperature growth of ZnO using the metal-organic process. Here excellent films have been obtained at temperatures as low as 400°C. The Zn vapor process using CO<sub>2</sub> has been greatly extended so that now insulating films have been obtained during initial growth. The key to this process has been the incorporation of lithium during growth by a unique vapor transport process. During the year a new growth process for epitaxial AlN was initiated and shows some promise for the growth of this difficult but important material.

The report first gives a general background into the materials and their historical technical problems and then summarizes the results obtained in this project. Details of the research are given in the appendices.

## 2.0 BACKGROUND

Zinc oxide and aluminum nitride have immense potential for use in the electronics industry. They are wide-band-gap, thermally-stable materials with high piezoelectric coupling coefficients. Layered media in which piezoelectric thin films are hetero-epitaxially deposited on a non-piezoelectric, low loss substrate such as sapphire, have unique properties and applications. These films on R-plane sapphire are of particular interest in this regard because the in-plane c axis orientations allow shear wave generation and are highly compatible with the growth of Si and other materials. Accordingly, numerous attempts have been made to achieve the  $(11\bar{2}0) \text{ 6mm}/(01\bar{1}2) \text{ Al}_2\text{O}_3$  heteroepitaxial system for ZnO and AlN.

### 2.1 ZnO

Various sputtering techniques have been employed to grow ZnO films with c axis perpendicular to the substrate with varying degrees of success.<sup>1,2</sup> Such films exhibited high resistivity but have the disadvantage of low growth rate and poor crystallinity compared to recent epitaxial films.

Epitaxial films of ZnO can be grown at high rates (100  $\mu\text{m/hr.}$ ) by chemical vapor transport or deposition.<sup>3</sup> However, these films are semiconduction, n-type, with an as-grown resistivity of  $\approx 1 \text{ ohm-cm}$ . This value is far too low for devices based on the piezoelectric or electro-optic properties of ZnO where a value of greater than  $10^6 \text{ ohm-cm}$

is necessary. Different growth systems have been investigated with the idea that a method yielding high resistivity and film quality may be discovered. However, low resistivity has always resulted and post-growth compensation has been considered to be unavoidable. The low resistivity is attributed to a departure from true stoichiometry of  $\text{ZnO}$ , with either interstitial zinc or oxygen vacancies acting as the donor. The higher stability of oxygen gas compared to zinc vapor and a difference in the formation energies of Zinc and Oxygen defects make it difficult to grow a stoichiometric crystal. Zinc oxide films are generally grown under low oxygen partial pressure in the presence of hydrogen and are found to be zinc-rich and thus donor-dominated. Even after post-growth lithium doping, the conductivity is still unacceptably high and n-type. It is seen that a moderately high temperature and  $p_{\text{O}_2}$  (partial pressure of oxygen) must be used in the lithium diffusion process in order to achieve high resistivity.<sup>3</sup> Direct contact of the lithium source ( $\text{LiOH}$  or  $\text{Li}_2\text{CO}_3$ ) is not desirable as it leads to corrosion of both  $\text{ZnO}$  and the sapphire substrate. The problem of attack has been solved by using vapor transport of lithium by keeping the lithium hydroxide source at a distance from the substrate by the use of a spacer.<sup>4</sup> All attempts to compensate the films are either of inferior quality or polycrystalline. Transport of non-valent metal atoms (eg.  $\text{Cu}$ , which would lead to compensation) is hard to achieve, and results in drastic morphology



changes when ever successful.

The other problems associated with growth of zinc oxide films are the difficulty of uniform nucleation, poor growth reproducibility and spurious nucleation. Chemosorption properties of ZnO can also become important for films with high surface areas to volume ratio. The surface layers can give rise to depletion layers and influence the defect distribution in the films and change the overall properties of the films. The use of hydrogen as a carrier gas assures low oxygen partial pressure, which promote growth of zinc-rich films, and hydrogen is known to act directly as a donor in ZnO.<sup>5</sup> On the other hand the resistivity of ZnO has been seen to increase in the presence of CO<sub>2</sub>. The formation of ZnO by the reaction of zinc vapor with CO<sub>2</sub> has been the subject of studies of formation of ZnO in the Zinc smelting process.<sup>6</sup> The Zn (v) /CO<sub>2</sub> reaction system was recently investigated at USC and resulted in the successful deposition of high resistivity epitaxial films.<sup>7</sup>

High resistivity was exhibited by the as-grown films, which degraded on exposure to atmosphere and handling during interdigital transducer fabrication. This made lithium compensation a necessary step before the films could be used for surface acoustic wave device applications. Compensation of the films during growth by lithium, improvements in the reactor design for better control of the process, and uniform nucleation have now been achieved.

Lithium as a foreign atom in zinc oxide shows

amphoteric behavior. It occupies both the zinc and the interstitial sites where it behaves as an acceptor and a donor respectively. It has been verified that, independent of  $p_{O_2}$ , large concentrations of Li always lead to a range in which the concentrations of lithium occupied zinc sites and interstitial sites are equal.<sup>8</sup> Thus lithium saturated samples prepared or treated under moderately oxidizing conditions show high resistivity.<sup>9</sup> Incorporation of lithium during growth has not been achieved by transport using agents such as carbon monoxide or hydrogen. Lithium oxide is a very stable compound and has a low vapor pressure even at high temperatures ( $10^{-8}$  mm Hg at  $1000^{\circ}\text{C}$ ). Thus it was found necessary to use a source of lithium oxide close to the substrate, in order to create a sufficiently high partial pressure of lithium oxide over the growing film. This method guarantees the saturation of the ZnO films with lithium, with the result that high as-grown resistivities can be achieved.

## 2.2 AlN

Aluminum nitride is of interest to microwave acoustic applications because the material exhibits a high SAW velocity of propagation when grown on R-plane sapphire. Although it has the same symmetry and growth habit as ZnO, AlN characteristically grows insulating but at much higher temperatures,  $1200^{\circ}\text{C}$ .

Details of a new AlN growth procedure are given in the next section.

### 3.0 PROGRESS

Major emphasis for this past year was on the growth of insulating ZnO by CVD techniques and the demonstration of a new AlN growth system. The ZnO work is summarized briefly below with greater detail left to the appendices. An effort on planar magnetron sputtering was supported under JSEP at USC and has given valuable information for any new ZnO sputtering system.

#### 3.1 Metal-Organic CVD

Epitaxial films have been deposited on sapphire by using the reaction of diethylzinc with  $\text{H}_2\text{O}/\text{H}_2$  and  $\text{N}_2\text{O}/\text{N}_2$  at temperatures of  $400^\circ\text{C}$  respectively. The results of this work were presented at the Los Angeles Meeting of the Electrochemical Society and will be published in the Aug. 1980 issue of the Electrochemical Society Journal. (See Appendix A)

#### 3.2 $\text{Zn(v)}/\text{CO}_2$ Process

Excellent quality epitaxial films have been achieved by using this reaction system (Appendix B). However, the resistivity of these films was low and made lithium diffusion necessary. This process has now been improved and modified to incorporate lithium during growth. High resistivity films can be grown by this process (Appendix C).

#### 3.3 $\text{ZnCl}_2/\text{O}_2$ System

The zinc-rich nature of the CVD grown films is often related to the fact that these films are grown under low oxygen activities. In order to increase the oxygen partial pressure during growth and use pure oxygen as one of the

components of the reaction system, one must choose a zinc compound as the other component of the reaction so as to limit the thermodynamic driving force to a reasonable value. Zinc chloride with its melting point at  $365^{\circ}\text{C}$  and boiling point at  $730^{\circ}\text{C}$ , seems to be the most suitable. Shiosaki, et al.<sup>10</sup> who studied the  $\text{ZnCl}_2\text{-O}_2$  system, although with a different motive, found that the system was critically dependent on the surface treatment of sapphire and always gave colored films. The color may be related to the fact that zinc chloride is not available in high purity. The other problem with  $\text{ZnCl}_2$  is its deliquescent nature. In view of this, we employed the reaction of  $\text{HCl}$  with hot zinc to produce zinc chloride in situ. An experimental arrangement similar to the one used for the  $\text{Zn (v)/CO}_2$  process was used. 5%  $\text{HCl}$  in  $\text{N}_2$  gas was passed over molten zinc at  $550^{\circ}\text{C}$  to produce zinc chloride. Films were grown at substrate temperatures between  $750^{\circ}\text{C}$  and  $950^{\circ}\text{C}$ . Although the continuous films produced on pre-sputtered substrates showed resistivities higher than  $10^6$  ohm-cm, the films showed lack of orientation and high surface roughness. In general, the growth system was highly irreproducible and growth rate was limited to  $10\text{ }\mu\text{m/hr}$ . It was concluded that this reaction system was distinctly inferior to the  $\text{Zn(v)/CO}_2$  system with lithium incorporation.

#### 3.4 AlN

Chemical vapor deposition appears to be the most attractive method for fabricating AlN films. CVD provides good control of growth parameters and a reasonable deposition

temperature of  $1200^{\circ}\text{C}$ . Metal-organic CVD growth using the TMA/ $\text{NH}_3$  reaction yields good quality epitaxial films at low growth rates. This process is limited to films up to a few microns thickness.<sup>11</sup> The aluminum chloride/ammonia CVD process has been the subject of various studies and appears to be promising for growth at high rates.<sup>12,13</sup> The problems associated with handling extremely hydroscopic  $\text{AlCl}_3$  have made this process impractical in the past, especially because very minute quantities of oxygen can give rise to aluminum oxide formation and poor AlN morphology. Thus the use of the HCl and hot aluminum reaction to produce  $\text{AlCl}_3$  is extremely attractive, but the following problems must be avoided by the careful design of the growth system.

i) Formation of AlN at the surface of the aluminum by back diffusion of  $\text{NH}_3$ , which can give rise to a crust of aluminum nitride which would impede the transport of  $\text{AlCl}_3$ .

ii) Reaction of  $\text{AlCl}_3$  with silica which can introduce oxygen into the system.

A schematic diagram of the growth set-up fabricated is shown in Fig. 1. The system is designed such that the substrate can be taken up to a temperature of  $1500^{\circ}\text{C}$ . The aluminum source is independently heated by a resistance furnace. An aluminum oxide injection tube is used to eliminate the possibility of reaction between  $\text{AlCl}_3$  and silica. The back diffusion of  $\text{NH}_3$  to the hot aluminum source should be a minimum in this design. The amount of oxygen and other impurities have to be kept low in this system for the growth of good quality films. Purified  $\text{H}_2$  and high purity  $\text{NH}_3$  are

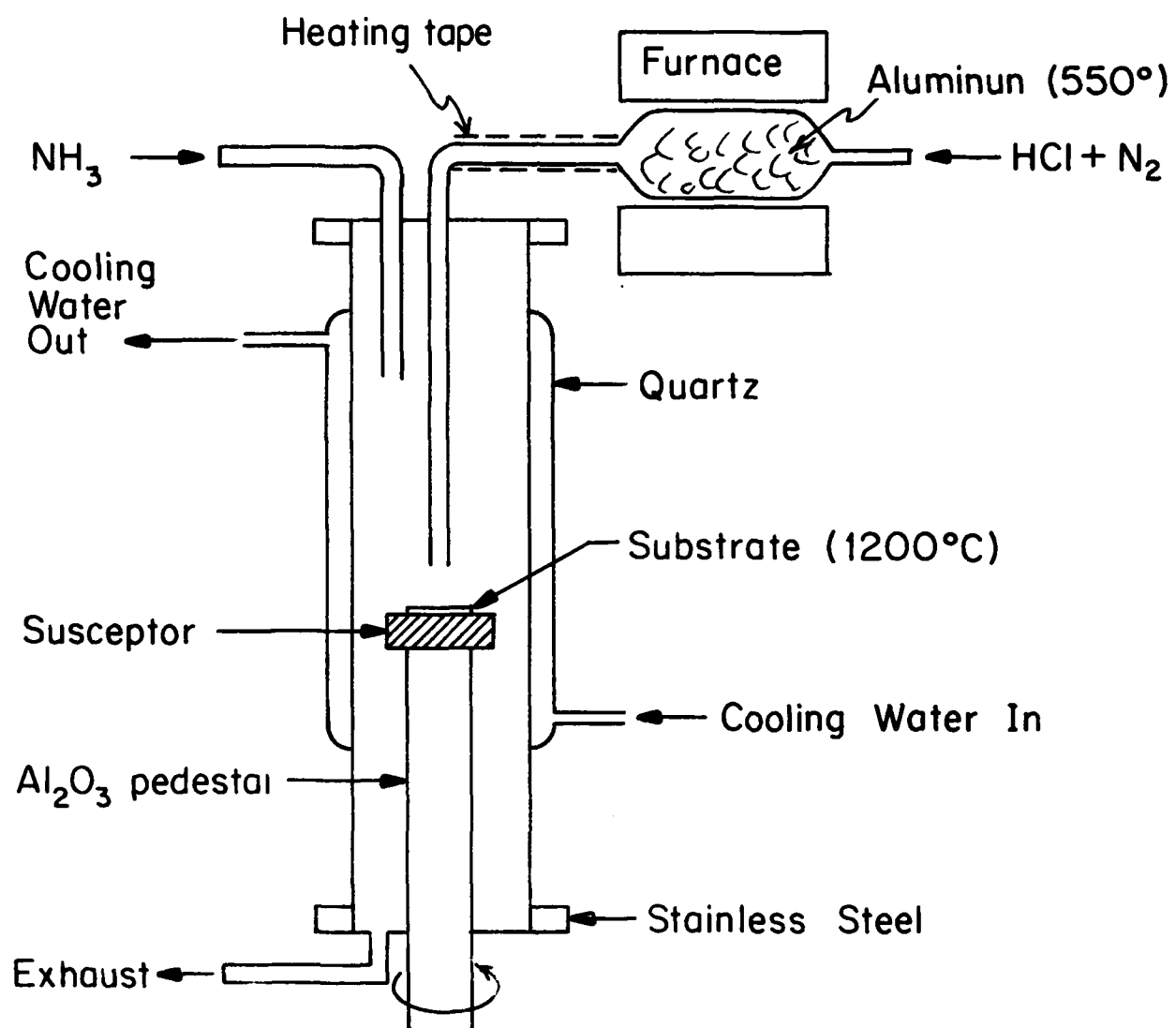


Figure 1. Growth system for the "hot aluminum" process in growing AlN.

therefore used.

### 3.5 Hydrothermal Growth

Two small research grade hydrothermal autoclaves have been acquired from Leco Corp. of State College, PA. These are LRA 150 RB pressure vessels, and have silver liners. A 3 inch diameter 3 zone vertical furnace has been set up with three temperature controllers, acquired from Eurotherm Corp., used to control the temperature profile of the furnace. The furnace temperature profile has been measured with the pressure vessel in place. Growth runs were not made because of lack of man-power and efforts spent on the more exciting ZnO CVD work.

#### 4.0 SUMMARY AND CONCLUSIONS

During the reporting period considerable progress was made in implementing and understanding the various thin film CVD growth systems. The CVD growth of insulating ZnO has been obtained for the first time using a novel vapor phase doping process and a new growth technique for epitaxial AlN has been introduced.

Because of the unique c-axis in the plane film orientation the ZnO films should be particularly suited to SAW and bulk shear wave devices.

In the future this research effort will be conducted within the Ames Laboratory at Iowa State University.



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Materials used were polished and cleaned (0112) sapphire (*R*-plane) substrates, nitrogen carrier gas obtained directly from liquid nitrogen boil-off, carbon dioxide of 99.999% purity, and zinc shot of 99.999% purity. Typical growth parameters are substrate temperature, 700–750 °C; zinc source temperature, 420–600 °C; center zone temperature, 900–1000 °C; gas flow rates,  $N_2$ : 0.5–2.1 l/min;  $CO_2$ : 0.6–4.5 l/min; growth rate, 0.1–0.5  $\mu\text{m}/\text{min}$ .

As grown films were transparent with very little roughness and excellent orientation of the surface features, as shown by the scanning electron micrograph of Fig. 2(a). However, initial experiments indicated that the growth tended to be nonuniform over a large area of the substrate, and that growth reproducibility was poor. This indicated that a problem of ZnO nucleation on sapphire exists in this system, as in the case of the other vapor transport systems. It must be born in mind that nucleation and growth in heteroepitaxial systems are different processes, and the same physical or chemical process may not give optimum conditions for both. In order to grow a good epitaxial film, one needs an initial layer which adheres well and is composed of a large number of nuclei per unit area. Planar magnetron rf sputtering was used to grow an initial 10-nm-thick layer of ZnO on the substrate,<sup>7</sup> using the following conditions: target material, ZnO or Zn (12 cm diameter); target-substrate spacing, 4.0 cm; gas composition, 80% Ar, 20%  $O_2$ ; chamber pressure, 5–10 Torr; rf power,  $\approx 50$  W; substrate temperature, 250 °C; exposure time, 45 sec.

The sputtering parameters and the nature of the presputtered films were not found to be critical. Subsequent CVD films grown on presputtered substrates were transparent with excellent surface finish suitable for a SAW device. Scanning electron micrograph of a typical as-grown film using sputtered film for nucleation is shown in Fig. 2(b). The films were single crystalline with (1120) ZnO|| (0112)  $Al_2O_3$  epitaxial relationship as confirmed by reflection electron diffraction as shown in Fig. 3.

The resistivity of the as-grown films was higher than those obtained from other CVD processes, and reached  $10^6$

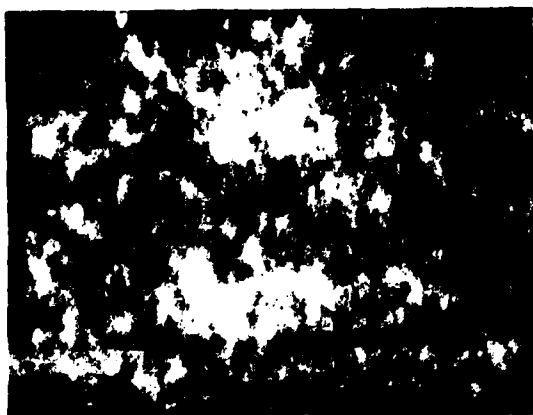


FIG. 3 Reflection electron diffraction pattern of ZnO on *R*-plane sapphire using 125-kV electron beam at glancing angle incidence.

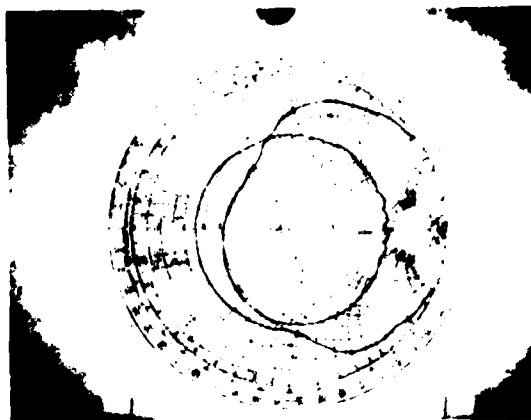


FIG. 4 Impedance plot for 15- $\mu\text{m}$  wavelength IDT on a 1.9- $\mu\text{m}$ -thick lithium-diffused ZnO film on sapphire

$\Omega$  cm on some samples. Resistivity, however, degraded on exposure to atmosphere at a faster rate than sputtered films,<sup>2</sup> and lithium diffusion was found to be necessary to hold the resistivity at  $10^6$   $\Omega$  cm or better.

In order to evaluate the electromechanical coupling coefficient, interdigital transducers (IDT) were fabricated on the films using the "lift-off" technique.<sup>8</sup> Figure 4 shows the impedance of a 15- $\mu\text{m}$ -periodicity IDT on a 1.9- $\mu\text{m}$ -thick ZnO film grown at 12  $\mu\text{m}/\text{h}$  growth rate. The film thickness to wave length ( $h/\lambda$ ) ratio of 0.13 is below the cutoff of all higher-order modes and corresponds to the local maximum value of the electromechanical coupling coefficient  $k^2$ .<sup>9</sup> The  $k^2$  value determined from the radiation resistance is 1.39%, which is higher than that obtained for the ZnO/ $H_2$ /HCl transport process ( $\approx 0.9\%$ )<sup>9</sup> and compares well with the theoretical calculation.<sup>10</sup>

In conclusion, the Zn(v)/ $CO_2$  CVD process for epitaxial growth of (1120) ZnO on (0112) sapphire is superior to other processes in yielding excellent films at a high growth rate for SAW and bulk mode shear wave applications, because of its simplicity, ease of operation, and moderate substrate temperature. Smooth surface finish and excellent reproducibility can be guaranteed using the presputtering technique. By proper use of doping during growth, passivation and handling techniques, the high as-grown resistivity may be used to advantage. Conditions for optimum growth rate, normal *c*-axis orientation on other substrates, lower temperature growth, and doping during growth are still under investigation.

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## APPENDIX B

# Growth of Epitaxial ZnO Thin Films by Organometallic Chemical Vapor Deposition

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## ABSTRACT

Organometallic chemical vapor deposition of ZnO on sapphire, using the reaction of diethylzinc with  $H_2O/H_2$ ,  $N_2O/N_2$ , and  $CO_2/H_2$  oxidizing gas systems, has been studied. Epitaxial films have been achieved at temperatures of 400° and 730°C, respectively, in the first two systems. The films have been characterized using scanning electron microscopy (SEM), reflection electron diffraction (RED), and surface acoustic wave techniques.

ZnO is one of the most versatile and useful thin film materials for acoustoelectric, acousto-optic, electro-optic, and photoconductive device applications (1). The heteroepitaxial system, (1120) ZnO/(0112)  $Al_2O_3$  with the c-axis of ZnO in the plane of the R-plane sapphire, is highly desirable for surface acoustic wave (SAW) device applications because of the high electromechanical coupling coefficient of ZnO and low acoustic wave propagation loss of sapphire. Furthermore, R-plane sapphire is the orientation used in silicon-on-sapphire (SOS) technology and for the growth of many III-V and II-VI compounds, implying the potential for integrating ZnO and semiconductor devices on a single substrate. Finally, substrates with good epitaxial quality surfaces are available commercially.

**Growth methods.**—RF sputtering is the most popular technique for ZnO thin film fabrication and recently planar magnetron sputtering has been successful in producing 5-10 micron thick films on glass substrates in an hours growth time (2, 3). These sputtered films have a tendency of growing with c-axis perpendicular to the substrate surface and only at very low growth rates ( $<100 \text{ Å/min}$ ) and high substrate temperatures ( $>500^\circ\text{C}$ ) have (1120) ZnO films on R-plane sapphire been achieved by sputtering (4). Growth of ZnO from the vapor phase has also been widely investigated. Most of the methods reported to date are essentially based on ZnO transport using the transport agents  $H_2/1\text{Cl}$  (5) and  $H_2/H_2O$  (6) or con-

trolled oxidation of zinc vapor. Growth rates of about  $1.2 \text{ μm/min}$  have been achieved at substrate temperatures around  $775^\circ\text{C}$ . However, because of the nucleation problems associated with the use of zinc vapor, film growth is nonuniform and nonreproducible. This problem can be solved by the introduction of a pre-sputtered layer of ZnO on the substrate. Using this technique with the  $ZnO/H_2O/O_2/H_2$  transport system, Ohnishi et al. (7) have grown films with excellent uniformity and surface finish. Growth rates of  $1 \text{ μm/min}$  were achieved at a rather high substrate temperature of  $575^\circ\text{C}$ . However, extensive corrosion of the quartzware takes place in all these transport systems. The corrosion problem has been mitigated by employing the reaction of zinc vapor and  $H_2O$  (8).

ZnO films grown by any of the vapor phase techniques show low resistivity, making postgrowth compensation necessary. Diffusion of lithium (and polishing to remove the damage due to etching by the lithium source) must be done before the films can be used for piezoelectric applications. Since the resistivity of ZnO films has been seen to increase in the presence of  $CO_2$  (1), the  $Zn(v)/CO_2$  reaction was recently investigated for the growth of ZnO films on sapphire (9). Here an as-grown resistivity of  $10^6 \text{ Ω-cm}$  resulted, but degraded on further process handling and exposure to the atmosphere.

**Organometallic growth.**—In recent years, the organometallic process for semiconductor thin film growth has received increasing attention, because of certain distinct advantages largely associated with the ease of handling the metal sources (10). Growth of compound

\*Electrochemical Society Active Member.  
 Key words: organometallic, CVD of ZnO, ZnO for SAW devices, ZnO thin films.

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semiconductor films using organometallic reactions has been reviewed by Manasevit (11) and the heteroepitaxial growth has been successful for a number of III-V semiconductor materials on various oxide substrates (10). The successful growth of II-VI compounds based on zinc has been reported by Manasevit and Simpson (12). The only organometallic growth method reported for the deposition of ZnO is by the decomposition of zinc propionate and zinc acetyl-acetonate (13). Oriented films were obtained at extremely low growth rates (27 Å/min.) on mica substrates.

In this paper, we report the results on the growth of ZnO thin films in R-plane sapphire, using the oxidation of diethylzinc,  $(C_2H_5)_2Zn$  (DEZ), by the three oxidizing gas mixtures,  $H_2O/H_2$ ,  $CO_2/H_2$ , and  $NO_2/N_2$  (14). Hydrogen, which plays a dominant role in the growth process, was used as the carrier for the  $H_2O$  and  $CO_2$  reaction systems and  $N_2$  was used for the DEZ/ $N_2O$  system.

### Experiment

**Growth system.**—Both horizontal and vertical quartz tube reactors were used in the present study as shown schematically in Fig. 1. The vertical gas flow system with substrate rotation proved to be advantageous in the DEZ/ $N_2O$  growth system, as more uniform films could be grown. In the case of the DEZ/ $H_2O$  reaction system, solid ZnO particles were formed on the inside walls of the injection tube. In the vertical geometry, these particles can be blown by the carrier gas onto the substrate, causing spurious growth problems. The horizontal growth system gave better quality films due to the absence of this problem. In both geometries the gas flow was at near normal incidence to the substrate surface. The temperature was monitored by a thermocouple with its tip placed inside a small hole in the susceptor. The injection tube-to-substrate distance was adjustable. The exhaust was connected to a scrubber through a rotary vacuum pump maintaining a pressure of about 400 Torr inside the reaction chamber.

The entire gas flow system for both the horizontal and the vertical reactors was assembled using stainless steel tubing, stainless steel bubblers for DEZ and deionized  $H_2O$ , and with provisions made for purging the system with nitrogen. The quartz reaction cham-

ber is 40 mm ID, 40 cm long tube. The susceptors used were 30 mm diam graphite disks capable of holding 20 mm square substrates.

Nitrogen gas was obtained directly from liquid nitrogen boil-off, and  $H_2$ ,  $N_2O$ , and  $CO_2$  were of four-nine purity. Electronic grade DEZ was chilled with melting ice to get better control over the flow rate (The vapor pressure of DEZ at 20°C is 15 Torr.)

**Substrate preparation.**—R-plane sapphire (3.8 cm diam and 1.23 mm thick) of epitaxial surface quality was purchased from Union Carbide. A standard polishing and cleaning procedure consisted of Syton (Monsanto) polishing for 10 min followed by cleaning with trichloroethylene, acetone, and methanol. Deionized water was used for the final wash before the dry nitrogen blow-off.

**Experimental procedure.**—To start a growth run, the reactor was evacuated and the carrier gas was admitted. The preparatory sequence continued by heating the substrate to the deposition temperature followed by introduction of the oxidizing gas. After about 5 min, growth was initiated by introduction of DEZ and continued for a specified time. After the growth run, the substrate was cooled slowly.

As-grown films were examined visually under an optical microscope and a small portion of the film was etched away with dilute HCl and the remaining film thickness measured across the etched step using a stylus-type profile meter (Dektak). Further physical characterization was carried out using SEM and RED.

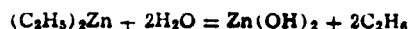
Electrical characterization consisted of a four-point probe resistivity measurement followed by capacitance and electromechanical coupling coefficient measurements using a surface acoustic wave interdigital electrode transducer.

### Results and Discussion

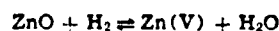
**Reactions.**—DEZ is an electron deficient compound with two vacant orbitals. The presence of these vacant orbitals available for bonding explains its high chemical reactivity. Thus, DEZ forms complexes easily with compounds containing free electron pairs. DEZ forms complexes at temperatures near ambient or higher with  $H_2O$ ,  $CO_2$ , and  $N_2O$  (15). The reactions of interest in the present study are:

#### 1. DEZ/ $H_2O$ / $H_2$ system (15)

At room temperature, in the gas stream

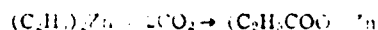


At the surface at high temperature (400°C)

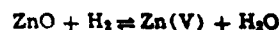


#### 2. DEZ/ $CO_2$ / $H_2$ system (16)

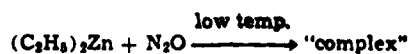
At 150°C, in the gas stream



At high temperature, on the substrate (500°C)



#### 3. DEZ/ $N_2O$ / $N_2$ system (18)



**Growth kinetics.**—Because of the formation of organo-zinc complexes for  $Zn(OH)_2$  in the DEZ/ $H_2O$  system at low temperature, it is necessary to keep the reactants separate until they are a short distance

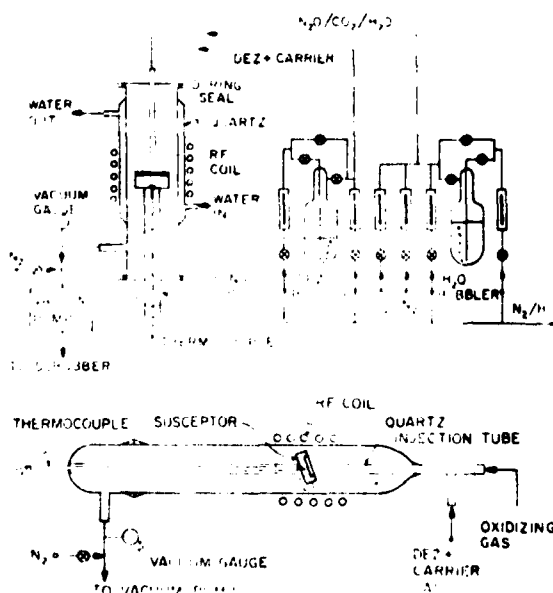


Fig. 1. Schematic diagram of the growth system used for ZnO OM CVD growth. (a) top: vertical geometry. (b) bottom: horizontal geometry.

Table I. Growth parameters and properties of ZnO films grown by OM CVD

Reaction system	Temperature, °C	Time, min	Flow rate, l/min	Pressure, Torr	Growth rate, Å/min	Optimum growth rate, Å/min
DEZ/H <sub>2</sub> O/N <sub>2</sub>	400	60	0.120	2.5	0.021	0.05
DEZ/CO <sub>2</sub> /N <sub>2</sub>	400	60	0.120	2.5	0.021	0.05
DEZ/N <sub>2</sub> O/N <sub>2</sub>	400	60	0.120	2.5	0.021	0.05

Reaction pressure: 2 Torr

away from the substrate. Homogeneity of mixing and density of the reactants uniform to the substrate is difficult to achieve. The reactor must be geometrically optimized to achieve growth uniformity and low pressure must be used in order to accelerate complex dissociation and removal of reaction products from the growth surface.

Table I shows the growth parameters for the three reaction systems. The rate of growth as a function of

temperature, with all other parameters being constant and equal to the optimum values given in Table I, is shown in Fig. 2. The optimum temperatures for the three systems are 400°C for the H<sub>2</sub>O/H<sub>2</sub> process, for the CO<sub>2</sub>/H<sub>2</sub> and 400°C for the N<sub>2</sub>O/N<sub>2</sub> process. The shapes of the curves indicate that the growth is kinetically controlled at low temperature because of the activation energy needed to dissociate ZnO(H<sub>2</sub>)<sub>2</sub> to the complex. At high temperature, the growth rate drops due to thermodynamic factors, including the instability of ZnO in the presence of hydrogen. In addition, the growth rate was observed to decrease as the DEZ/oxidizing gas ratio was increased and at very high DEZ concentration growth stopped in all the three reaction systems. This indicated poisoning of the growth surface by excess complex molecules. Thus, the desorption of large organic species may be the rate-limiting step under such conditions. Figure 3 shows the dependence of the growth rate on the oxidizing gas flow rate with constant flow rates of other gases (equal to the optimum values of Table I). Maxima are observed in each case. Thus adsorption of H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>O by the ZnO surface may also lead to a drop in the growth rate.

**Growth morphology.**—Films obtained with the DEZ/H<sub>2</sub>O/H<sub>2</sub> process were pale white translucent with a rough surface. The SEM micrograph for a typical film, shown in Fig. 4, does not reveal any obvious

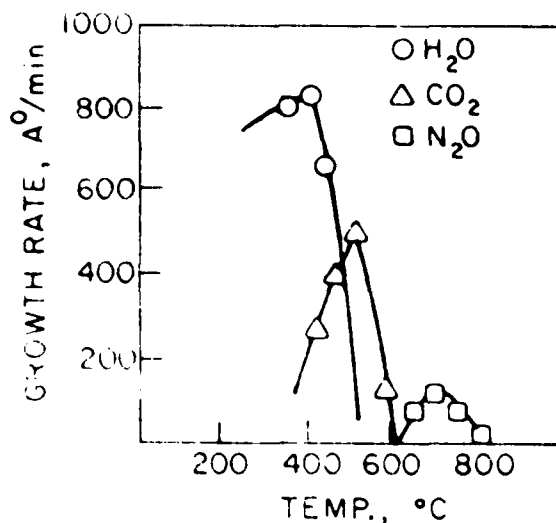


Fig. 2. Growth rate as a function of temperature, with other parameters constant at the optimum values given in Table I.

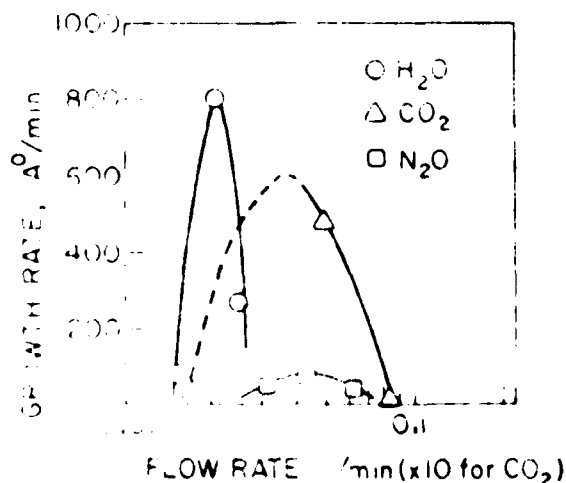


Fig. 3. Growth rate as a function of flow rate, with other parameters constant at the optimum values given in Table I.

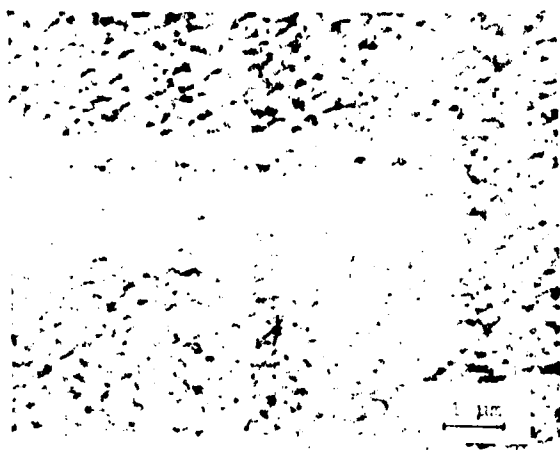


See attached figure.



Fig. 4. SEM micrograph for a 2-μm-thick ZnO film grown at 400°C by the DEZ/H<sub>2</sub>O/H<sub>2</sub> process, with other parameters constant at the optimum values given in Table I.

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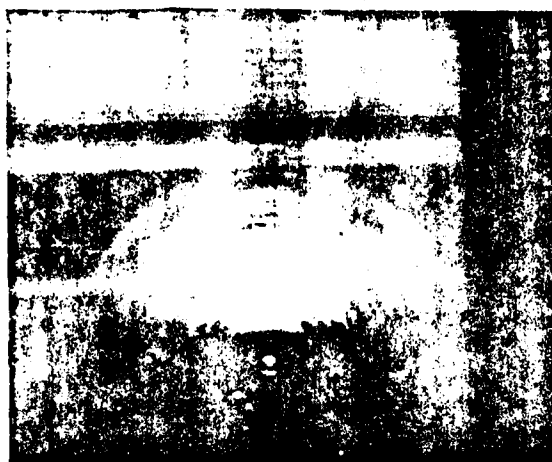
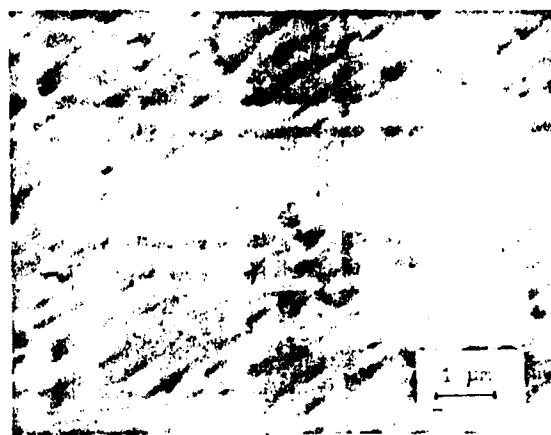


Fig. 5. SEM/RED for a 2  $\mu\text{m}$  thick ZnO film grown at 500°C by the DEZ/CO<sub>2</sub>/H<sub>2</sub> growth system.

alignment of crystallites, although the RED confirms an oriented film. Films grown by the DEZ/CO<sub>2</sub>/H<sub>2</sub> system were polycrystalline (Fig. 5). Films grown by the N<sub>2</sub>O/N<sub>2</sub> process were transparent with very smooth surfaces and the SEM/RED data, Fig. 6, show that the crystallites are aligned along the c-axis of ZnO crystallites in the R-plane sapphire. ZnO has a marked tendency of growing fast along the c-axis and it appears that in the presence of H<sub>2</sub> any needles that are not in the growth plane become unstable. In the DEZ/N<sub>2</sub>O/N<sub>2</sub> system, because of the absence of hydrogen, spurious growth can become important. Thus, if the arrival rate of the complex is increased by reducing the distance between the injection tube and the substrate, growth rate increases and spurious growth, with hexagonal needles growing out of the plane, results as shown in Fig. 7. Thus, the growth rates must remain low in order to retain epitaxy.

**Electrical characterization.**—Resistivity of the films was measured by the four-point probe method. The results are listed in Table II. Films grown by using CO<sub>2</sub> have a high resistivity of 10<sup>4</sup>  $\Omega\text{-cm}$  and those grown by H<sub>2</sub>O and N<sub>2</sub>O reactions exhibit low resistivity. For SAW applications, a resistivity of greater than 10<sup>4</sup>  $\Omega\text{-cm}$  is necessary. Aluminum diffusion for increasing the resistivity was carried out for some films, by coating the films with Li<sub>2</sub>CO<sub>3</sub> solution and heating them at 400°C for 12 hr. The film had to be polished after the diffusion to remove the surface damage due to the etching of Li<sub>2</sub>CO<sub>3</sub>.



See attached figure.

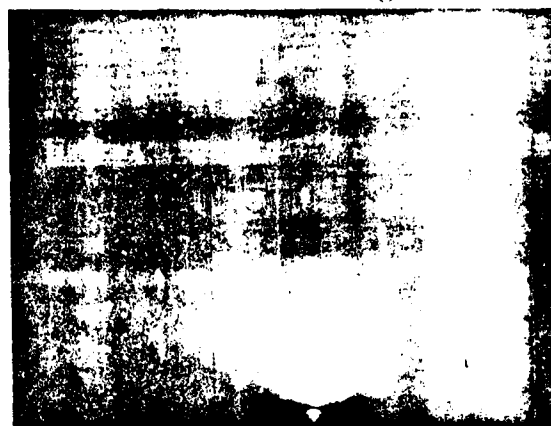
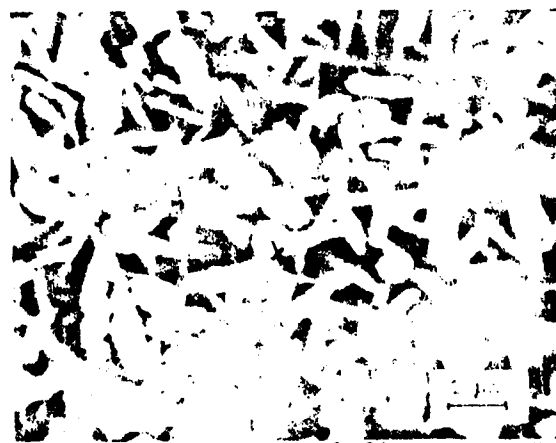


Fig. 6. SEM/RED for a 1.5  $\mu\text{m}$  thick ZnO film grown at 730°C by the DEZ/N<sub>2</sub>O/N<sub>2</sub> growth system.

Aluminum interdigital transducers (IDT) of 15  $\mu\text{m}$  wavelength were fabricated on the film surface using the "lift-off" technique (17). The impedance of the IDT was then measured as a function of frequency using an HP8410 network analyzer. The SAW electro-mechanical coupling coefficient ( $K^2$ ) for the c-axis propagating ZnO/Al<sub>2</sub>O<sub>3</sub> structure was then calculated using the expression (18)



See attached figure.

Fig. 7. SEM picture of film grown by the N<sub>2</sub>O/N<sub>2</sub> process under high flux conditions, showing spurious growth.

Table II. Properties of ZnO films grown by OM-CVD

Process	Electrical resistivity, $\Omega\text{-cm}$		SAW properties			
	As-grown	After la diffusion	Film thickness, $\mu\text{m}$	Resonant freq., MHz	$t/\lambda$	Coupling coef. $K^2$
DEZ/H <sub>2</sub> O/H <sub>2</sub>	1-10	>10 <sup>6</sup>	1.0	351.17	0.067	0.22%
DEZ/N <sub>2</sub> O/N <sub>2</sub>	10 <sup>-</sup>	>10 <sup>6</sup>	1.2	343.43	0.08	0.61%

\* After polishing, the film thickness was uniform within  $\pm 0.1 \mu\text{m}$  over an area of  $1 \times 2 \text{ cm}$ .

$$K^2 = \pi^2 f_0 R_a C_f / 2$$

where  $f_0$  = resonant frequency,  $R_a$  = radiation resistance, and  $C_f$  = capacitance/finger pair.

The coupling coefficient and other relevant parameters are tabulated in Table II. The films grown by the H<sub>2</sub>O and N<sub>2</sub>O reaction systems were found to be piezoelectric as expected from the RED data. The films grown by the CO<sub>2</sub> process were found to be of poor quality, and several attempts to measure the SAW properties were unsuccessful. For the DEZ/N<sub>2</sub>O/N<sub>2</sub> process, a  $K^2$  value of 0.61% at a thickness to wavelength ratio ( $t/\lambda$ ) of 0.08 was determined which is better than the value obtained by Pizzarello using the ZnO/HCl/H<sub>2</sub> closed-space transport process (19), and is comparable to the theoretical value obtained by Lakin and Penunuri (20). The coupling coefficient for films grown by the DEZ/H<sub>2</sub>O/H<sub>2</sub> process is lower (0.22% at  $t/\lambda = 0.067$ ), but reasonable for a low growth temperature of 400°C.

### Conclusion

The organometallic reaction systems using the reaction of DEZ with H<sub>2</sub>O/H<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub>, and N<sub>2</sub>O/N<sub>2</sub> were investigated and these show promise as low temperature growth techniques for epitaxial ZnO thin films. The films were evaluated by SEM, RED, and by surface acoustic wave measurements. The films grown by the H<sub>2</sub>O and N<sub>2</sub>O reactions at temperatures of 400- and 739°C showed electromechanical coupling coefficients of 0.22% at a thickness to wavelength ( $t/\lambda$ ) ratio of 0.067 and 0.61% at  $t/\lambda = 0.08$ , respectively.

Methods to increase the growth rate and the resistivity are under investigation.

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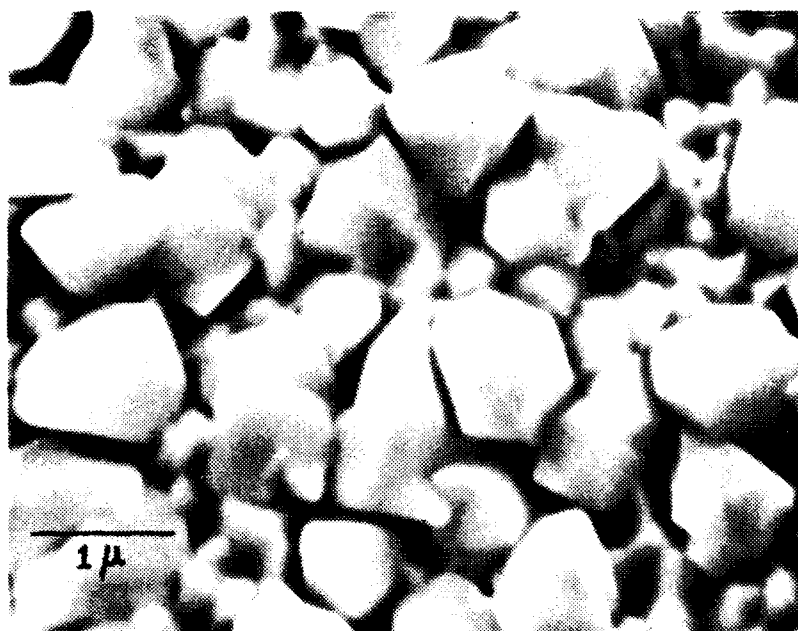
Any discussion of this paper will appear in a Discussion Section to be published in the June 1981 Journal. All discussions for the June 1981 Discussion Section should be submitted by Feb. 1, 1981.

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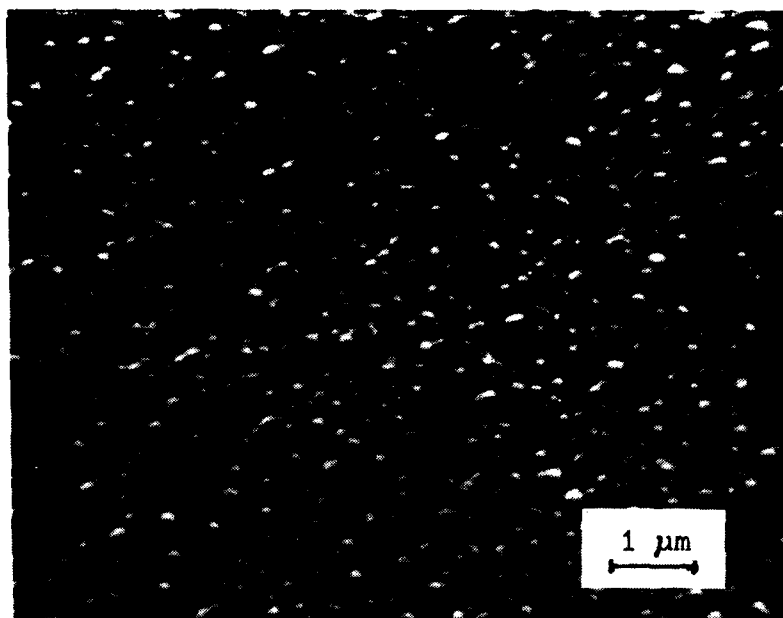
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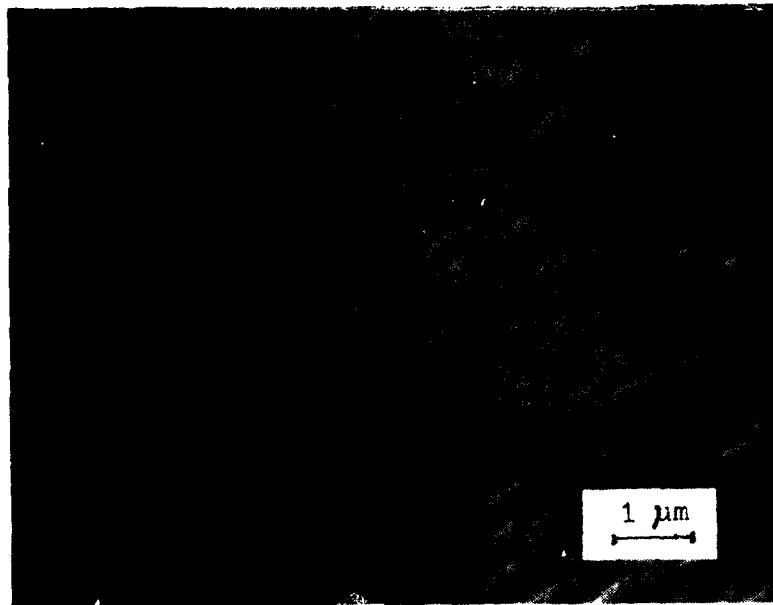




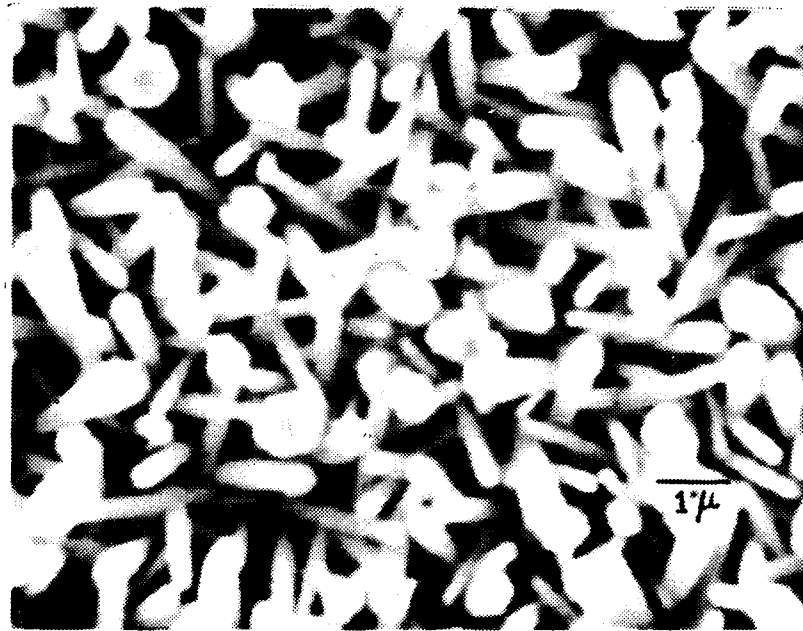
4. SEM/RED for a 2 micron thick ZnO film grown at 400°C by the DEZ/H<sub>2</sub>O/H<sub>2</sub> growth process.



5. SEM/RED for a 2 micron thick ZnO film grown at 500°C by the DEZ/CO<sub>2</sub>/H<sub>2</sub> growth system.



6. SEM/RED for a 1.5 micron thick ZnO film grown at 730°C by the DEZ/N<sub>2</sub>O/N<sub>2</sub> growth system.



7. SEM picture of film grown by the  $\text{N}_2\text{O}/\text{N}_2$  process under high flux conditions, showing spurious growth.

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