

thank Prof. N. Min of the Department of Control and Instrumentation Engineering of Korea University and Dr. D. Oh of Electronics and Telecommunications Research Institute for generous donation of Si wafers.

References

1. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1046 (1990); C. Pickering *et al.*, *J. Phys. C.*, **17**, 6535 (1984).
2. L. T. Canham, M. R. Houlton, W. Y. Leong, C. Pickering, and J. M. Keen, *J. Appl. Phys.*, **70**, 422 (1991).
3. K. A. Littau, A. Mulle, P. J. Szajowski, and L. E. Brus, "Extended abstracts of the 182nd Electrochemical Society Meeting", Toronto, Canada, 825 (1992).
4. A. Nakajima, T. Hakura, Satoru Watanabe, Y. Sugita, Y. Nara, and N. Nakayama, "Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials", Tsukuba, Japan, 472 (1992).
5. T. V. Buuren, Y. Gae, T-Tiedje, J. R. Dahn, and B. M. Way, *Appl. Phys. Lett.*, **60**, 3013 (1992).
6. P. McCord, S.-L. Yau, and A. J. Bard, *Science*, **257**, 68 (1992).
7. V. V. Doan and M. J. Sailor, *Science*, **256**, 1791 (1992).
8. C. W. Sheen, J.-X. Shi, Jan Martensson, A. N. Parikh, and D. L. Allara, *J. Am. Chem. Soc.*, **114**, 1514 (1992).
9. T. Unagami and M. Seki, *J. Electrochem. Soc.*, **125**, 1339 (1978).
10. J. M. Lauehaas, G. M. Credo, J. L. Heinrich, and M. J. Sailor, *J. Am. Chem. Soc.*, **114**, 1911 (1992).
11. D.-I. Kim, M.-K. Oh, and C.-W. Lee, unpublished results.

Preparation of Aluminum Nitride Thin Films Using Single Precursor OMCVD

Joon T. Park*, June-Key Lee, Sehun Kim,
Myung Mo Sung†, and Yunsoo Kim†

*Department of Chemistry,
Korea Advanced Institute of Science and Technology,
Taejeon 305-701

†Advanced Materials Division,
Korea Research Institute of Chemical Technology,
Taejeon 305-606

Received October 12, 1992

The preparation of aluminum nitride (AlN) thin films has received much attention due to its potential applications in the electronic and optoelectronic devices.¹ AlN has the wurtzite crystal structure, a large band gap of about 6.2 eV, a high decomposition temperature (*ca.* 2400°C), and good chemical stability. It is a promising material for electronic substrates such as passivation and dielectric layers, protective coatings, surface acoustic wave devices, and optical devices.¹ Several techniques have been employed for the preparation of AlN thin films including conventional organometallic chemical vapor deposition (OMCVD),² molecular beam epitaxy (MBE),³ and single precursor OMCVD.⁴ The single precursor

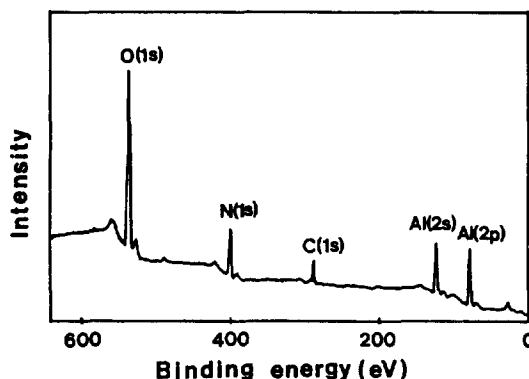


Figure 1. XPS spectrum of Film II deposited at 500°C.

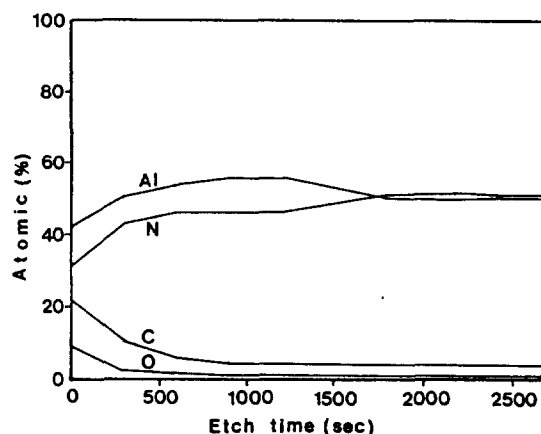


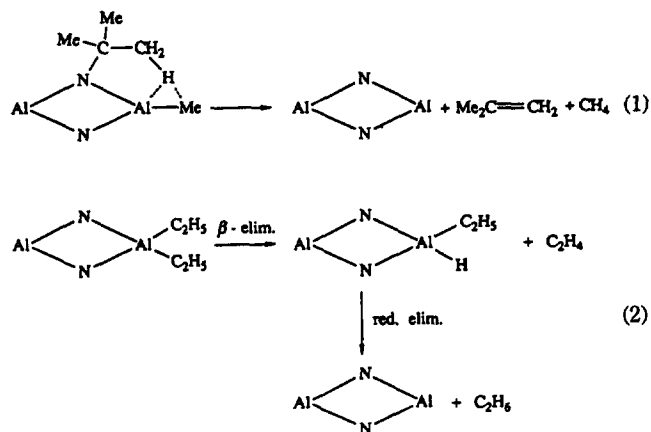
Figure 2. Auger depth profile of Film II deposited at 500°C.

OMCVD has been shown to have a number of important advantages over the conventional CVD processes.⁵ Several groups^{4,6} recently reported the preparation of group III-V semiconductor films using the single precursor OMCVD method, especially, at low temperatures ($\leq 500^\circ\text{C}$) in order to be compatible with current semiconductor device technology and to prevent interdiffusion of layers. In this communication we report the preparation and characterization of AlN thin films by single precursor OMCVD with two amidoalane dimers, $[\text{Me}_2\text{Al}(\mu\text{-NHA'Bu})_2]$ (**1**) and $[\text{Et}_2\text{Al}(\mu\text{-NH'Bu})_2]$ (**2**).

The single precursors, **1**⁷ and **2**,⁸ were prepared and purified by sublimation as previously described. Film growth conditions involved the use of a hot-wall CVD apparatus. Silicon (100) wafers ($10 \times 10 \text{ mm}^2$) were used as substrates.⁹ The base and the steady state pressures of the CVD reactor were $(3\text{--}5) \times 10^{-5}$ and $(1\text{--}2) \times 10^{-4}$ Torr, respectively. AlN films were grown in the temperature range 200–800°C with both precursors. The optimum temperatures for the film growth with precursors **1** and **2** were found to be 650°C (Film I) and 500°C (Film II), respectively.¹⁰ Atomic compositions of the films were determined by X-ray photoelectron spectroscopy (XPS) and a typical XPS spectrum of the AlN film (Film II) is shown in Figure 1. The respective Al 2s, Al 2p, N 1s, C 1s, and O 1s peaks at 120.5, 74.0, 396.7, 285.0, and 531.7 eV¹¹ reveal the Films I and II to have comparable amounts of Al and N with surface contamination of carbon and oxygen.¹² Auger depth profile studies were performed using argon ion sputtering in which the Al, N, C, and O

atomic concentrations were monitored as a function of sputtering time (etch rate of $\sim 100 \text{ \AA}$) as shown in Figure 2 for Film II. The results indicate close to a one to one ratio of aluminum to nitrogen in the bulk of the film with carbon around 5% and oxygen around 1-2%. The surface of the film contained appreciably higher amounts of oxygen and carbon. The FTIR spectra of the films both I and II showed a single, strong band at 680 cm^{-1} which is due to the Al-N stretching vibration.¹³ The thickness of the films was measured by scanning electron microscopy (SEM) of the cross-sectioned AlN-substrates: Film I ($3.8 \text{ }\mu\text{m}$, growth time 22 h, growth rate $1700 \text{ \AA/h}$) and Film II ($1.0 \text{ }\mu\text{m}$, growth time 10 h, growth rate $1000 \text{ \AA/h}$). The films were found to exhibit a columnar structure with good adherence to the substrate. Their morphology studied by SEM revealed that they are amorphous.

The gaseous products evolved during pyrolysis of precursors **1** (650°C) and **2** (500°C) were trapped in a liquid N_2 -cooled vessel and analyzed by gas chromatography. The analysis from precursor **1** reproducibly showed 76% methane and 15% isobutene as the major hydrocarbons in addition to smaller quantities of C_2 and C_3 products, whereas that from **2** revealed 60% ethane, 30% ethylene and a very small amount of C_1 , C_3 and C_4 products. The results would propose possible decomposition mechanisms of **1** and **2** for the deposition of the AlN thin films. The primary mechanism for **1** (Eq. (1)) may involve interaction of the aluminum atom



with the C-H bond of a 'Bu group followed by cleavage of N-C bond to form isobutene and elimination of methane from aluminum, as was proposed in thermal decomposition studies of $[\text{Me}_2\text{Ga}(\mu\text{-As'Bu}_2)]_2$.^{6a,14} A plausible mechanism for **2** (Eq. (2)) involves β -hydrogen elimination from an ethyl group giving ethylene and subsequent elimination of ethane from aluminum, which is well preceded in organometallic chemistry¹⁵ although the fate of the 'Bu group is not clear at the moment.

The present work indicates that the use of single precursors, dimeric amidoalanes, is promising because they achieve low-temperature production of AlN thin films. The ethyl substituent on aluminum in **2** apparently helps to lower the deposition temperature by about 150°C compared to the methyl analogue **1**, presumably, due to the low energy β -elimination pathway for the ethyl groups. We are currently carrying out the analysis of the volatile products from **1** and

2 released during OMCVD processes to address clear mechanistic pathways. Further effort to grow epitaxial AlN films is also in progress.

Acknowledgement. We are grateful to Korea Advanced Institute of Science and Technology for the partial financial support of this research. Additional support to Y. Kim was provided by the Ministry of Science and Technology.

References

1. L. M. Sheppard, *Ceramic Bulletin*, **69**, 1801 (1990).
2. (a) M. T. Duffy, C. C. Wang, G. D. O'Clock, Jr., S. H. McFarlane, and P. J. Zanzucchi, *J. Electron. Mater.*, **2**, 359 (1973); (b) T. M. Mayer, J. W. Rogers, Jr., and T. A. Michalske, *Chem. Mater.*, **3**, 641 (1991).
3. S. Yoshida, S. Misawa, and A. Itoh, *Appl. Phys. Lett.*, **26**, 461 (1975).
4. (a) D. C. Boyd, R. T. Haasch, D. R. Mantell, R. K. Schultze, J. F. Evans, and W. L. Gladfelter, *Chem. Mater.*, **1**, 119 (1989); (b) L. V. Interrante, W. Lee, M. McConnell, N. Lewis, and E. Hall, *J. Electrochem. Soc.*, **136**, 472 (1989); (c) K.-L. Ho, K. F. Jensen, J.-W. Hwang, W. L. Gladfelter, and J. F. Evans, *J. Crystal Growth*, **107**, 376 (1991).
5. A. H. Cowley and R. A. Jones, *Angew. Chem. Int. Ed. Engl.*, **28**, 1208 (1989), and references therein.
6. (a) A. H. Cowley, B. L. Benac, J. G. Ekerdt, R. A. Jones, K. B. Kidd, J. Y. Lee, and J. E. Miller, *J. Am. Chem. Soc.*, **110**, 6248 (1988); (b) J. E. Miller and J. G. Ekerdt, *Chem. Mater.*, **4**, 7 (1992); (c) J.-W. Hwang, S. A. Hanson, D. Britton, J. F. Evans, K. F. Jensen, and W. L. Gladfelter, *Chem. Mater.*, **2**, 342 (1990).
7. A.-A. I. Al-Wassil, P. B. Hitchcock, S. Sarisaban, J. D. Smith, and C. L. Wilson, *J. Chem. Soc., Dalton Trans.*, 1929 (1985).
8. R. E. Bowen and K. Gosling, *J. Chem. Soc., Dalton Trans.*, 964 (1974).
9. The substrates were cleaned by washing with tetrachloroethane, ethanol, deionized water, diluted (20%) hydrofluoric acid, and deionized water in sequence.
10. The optimum temperatures were determined by characterization of films deposited at various temperatures between $200\text{--}800^\circ\text{C}$, which showed the best quality of films in terms of atomic compositions.
11. (a) J. A. Taylor and J. W. Rabalais, *J. Chem. Phys.*, **75**, 1735 (1981); (b) C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, "Handbook of X-ray photoelectron Spectroscopy", Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, 1979.
12. The surface contained considerable oxygen and carbon contamination which is expected from handling and transporting the films.
13. L. Xinjiao, X. Zechuan, H. Ziyu, C. Huazhe, S. Wuda, C. Zongcai, Z. Feng, and W. Enguang, *Thin Solid Films*, **139**, 261 (1986).
14. J. E. Miller, M. A. Mardones, J. W. Nail, A. H. Cowley, R. A. Jones, and J. G. Ekerdt, *Chem. Mater.*, **4**, 447 (1992).
15. P. Zanella, G. Rossetto, N. Brianese, F. Ossola, and M. Porchia, *Chem. Mater.*, **3**, 225 (1991).