PVT Growth of Bulk AlN Crystals with Low Oxygen Contamination

M. Bickermann[1], B. M. Epelbaum[1,2], A. Winnacker[1]
[1]Department of Materials Science 6, University of Erlangen-Nürnberg, Martensstr. 7, D-91058 Erlangen.
[2]SiCrystal AG, Paul-Gossen-Str. 100, D-91052 Erlangen.
Contact author: matthias.bickermann@ww.uni-erlangen.de (Matthias Bickermann)

Bulk crystals of AlN have a great potential to provide a better substrate for GaN based electronic devices than currently available sapphire and SiC. Very recently the shortest stimulated emission of 258 nm reported up to date in semiconductor materials have been observed under optical excitation in AlGaN/AlN-based quantum well structures grown over single-crystal bulk AlN substrates by MOCVD [1].

Despite a number of promising crystal growth studies of AlN [2-5] published after the pioneering work of Slack and McNelly on sublimation-recondensation growth of AlN [6], available crystals are still too small to allow successful substrate applications. The largest crystals of AlN reported have been grown by direct sublimation (PVT method) and were about 10 mm in size. The small sizes of the AlN crystals show indirectly that AlN must grow very slowly at 1900-2400°C and ambient pressures below 1 bar. The reason for this has been a subject of much controversy. Two major issues, a small sticking coefficient of nitrogen molecules on the growing surface and specific mass transport conditions causing AlN charge depletion at low ambient nitrogen pressures [7], are discussed.

On the other hand, oxygen is the most common impurity in semiconductor nitrides. It is known to influence electrical, optical and thermal properties. For AlN in particular, oxygen acts as a deep donor leading to a broad UV absorption band in the range 3.5…5.5 eV [8]. Additionally, oxygen incorporation during PVT growth of AlN bulk crystals leads to formation of aluminum vacancies, which act as scattering centers for phonons. Hence, low oxygen contamination is a prerequisite for obtaining high thermal conductivity in AlN [9]. The role of oxygen during sublimation-recondensation (PVT) growth of bulk AlN crystals has been paid little attention by now.

Our current study was performed to establish a PVT growth process for the preparation of bulk AlN with low oxygen content, taking into account possible rate-limiting steps in PVT processing of AlN including mass transport in the gas phase, interfacial growth kinetics, and oxygen contamination during growth.

Crystal growth experiments were conducted in a proprietary designed growth reactor provided with tungsten heating elements capable up to 2500°C in the atmosphere of high-purity nitrogen. The source material was ceramic grade AlN powder with 99.5% purity (oxygen as main residual impurity). Excessive supersaturation and quick material transport in combination with insufficient crucible integrity were found to be the only size-limiting factors in PVT growth of AlN. Contrary, the sticking coefficient of nitrogen at growth temperatures of over 2000°C was found to be in the order of $10^{-2}\dots10^{-3}$, allowing growth rates exceeding 2…3 mm/h. Hence, the problem that is to be solved to increase the size of AlN single crystal is the proper choice of crucible material and design, i.e. it is a pure technological obstacle.

Sublimation products were characterized using optical microscopy, SEM and powder X-ray diffraction. It was found, that at growth temperatures exceeding 2000°C, oxygen, even at high concentrations, acts as an effective transporting agent, but does not produce any oxynitrides and does not alter the AlN crystal structure. Therefore the most troubling effect of oxygen is seed contamination with small AlO_xN_y and AlN particles at the early stage of growth (heating stage) because of oxygen assisted transport at low temperatures of 1500-1700°C. The temperature reversal method [10] where the seed was partially resublimed after bringing it to working temperature has been successfully used to avoid seed contamination.

AlN boules with one inch in diameter and up to 10 mm in height containing single-crystalline areas larger than 5x5 mm^2 have been grown. Chemical analysis showed an oxygen content of lower than 80 ppm wt, equaling a concentration of 1×10^{19} cm^{-3} in the crystal, the lowest oxygen contamination for bulk AlN reported up to date. The low optical absorption coefficient of $\alpha \approx 30$ cm^{-1} obtained in the visible/near UV range and high thermal conductivities of $\lambda = 186$ W / m K at room temperature measured with the laser flash method also confirm that the oxygen content is at low 10^{19} cm^{-3}.

[1] R. Gaska, C. Chen, J. Yang et. al., Applied Physics Letters 81 (2002) 4658
[2] C.M. Balkas, Z. Sitar, T. Zheleva, et.al. J. Cryst. Growth 179 (1997) 363
[3] L. Liu, B. Liu, Y. Shi and J.H. Edgar, MRS Internet J. Nitride Semicond. Res. 6,7 (2001)
[4] R. Schlesser, Z. Sitar, J. Cryst. Growth 234 (2002) 349
[5] L.J. Schowalter, J.C. Rojo, G.A. Slack et.al. J. Cryst. Growth 211 (2000) 78
[6] G.A. Slack, T.F. McNelly, J. Cryst. Growth 34 (1976) 263
[7] S.Yu. Karpov, Yu.N. Makarov, M.S. Ramm, MRS Internet J. Nitride Semicond. Res. 2,45 (1997)
[8] J. Pastrnak and L. Roskovcova, phys. stat. sol. 26 (1968) 591
[9] G. A. Slack, R.A. Tanzilli, R.O. Pohl and J.W. Vandersande, J. Phys. Chem. Solids. 48 (1987) 641
[10] M. Schieber, I. Beinglass, G. Dishon and A. Holzer, in: Crystal Growth and Materials (1976) eds. E. Kaldis and H. J. Scheel (North Holland, Amsterdam, 1977), p. 280