Materials Science Forum Vols. 389-393 (2002) pp. 1445-1448

Sublimation Growth of Bulk AlN Crystals: Materials Compatibility and Crystal Quality

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Keywords: AlN Single Crystal, AlN-SiC Mixed Crystals, Bulk Growth, Crucible Material, Sublimation Growth

Abstract. The main problem to be solved for stable growth of bulk pure AlN is the use of a suitable crucible material. Our analysis of the AlN sublimation growth process support the conclusion made by Slack and McNelly that tungsten is the best choice. However, in the real growth reactor tungsten must be combined with other materials to ensure flexible design and sufficient lifetime of the whole system. Compatibility of tungsten with other high-temperature structural and seed materials such as graphite, AlN and SiC is the topic of the present research.

Introduction. Perspectives of bulk AlN crystal growth are attracting much interest, as AlN wafers would be a nearly ideal substrate for nitride based electronic and optoelectronic devices due to small lattice mismatch with GaN, similar coefficient of thermal expansion and high electrical resistivity. Since the pioneering work of Slack and McNelly [1] the problem of chemical compatibility of materials used in the growth cell was recognized as the key issue in bulk AlN growth. Various crucible materials such as graphite and SiC coated graphite, nitrides (TiN, Ta_2N) and high-melting metals (W, Re, W–Re alloys) have been tested. However, AlN crystals grown are still limited in size and contain impurities (the latter is evidenced by crystal coloration). In this work, a systematic investigation of the compatibility of different materials in the reactor system was made and the results are discussed in terms of growth unit integrity, process stability and material quality.

Experimental. Crystal growth experiments were conducted in a resistively heated furnace using graphite or tungsten heating elements in the temperature range of 1800–2200°C, see Fig. 1. The source material was commercially available AlN powder (99%, CHEMPUR, Germany), aluminum and oxygen in form of Al_2O_3 being the main residual impurities. Seed plates of 10mm x 10mm were made of tungsten foil or cut from on axis 6H-SiC crystals grown in our laboratory. Growth was performed in an atmosphere of pure nitrogen and $N_2 + H_2/NH_3$ mixtures with pressures in the range of 50–750 mbar. Material combinations listed in Table 1 were tested under different temperatures and the use of various ambient gas compositions.

Table 1. Material combinations (arrangements) used in the model AlN reactor system

N	Crucible	Heater	Isolation
1	Dense graphite	Graphite	Porous graphite
1a	Silicon carbide coating	Graphite	Porous graphite
2	Tungsten	Tungsten	Tungsten
2a	Tungsten	Tungsten	AlN ceramics
3	Tungsten	Graphite	Porous graphite

The first two arrangements 1 and 1a represent 'standard' high-temperature material combinations based on graphite. The primary challenge with a 'pure graphite ambient' (arrangement 1) was crucible permeability for aluminum vapor and seed surface graphitization at T > 2000°C. Aluminum carbide vapor pressure was found to be sufficiently higher than that of AlN. Hence the main part of the charge was consumed in the reaction with carbon and only very limited growth of AlN islands on the SiC seed occurred. However, carbon contamination of the crystal was kept at a relatively low level. In the beginning of the process the carbothermic reduction of aluminum oxide film according to the reaction $Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ on the surface of AlN particles is very useful for the preparation of an oxygen-free AlN powder charge.

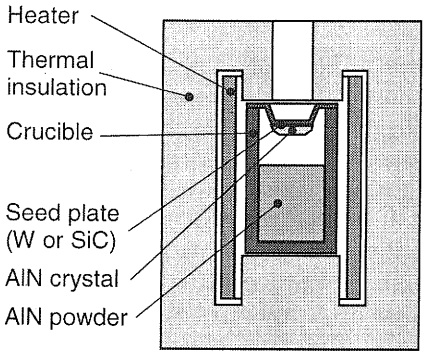

Fig. 1. Schematic of the growth unit

Coating of the graphite with a dense, 150–200 μm thick SiC layer (arrangement 1a) decreases the loss of aluminum only slightly. Similar to the results of Balkas et al. [2] SiC coating was found to be unstable already at T > 1950°C. According to our observations, equilibrium vapor pressures of the species in the system AlN–SiC are higher than in the respective 'pure' systems (AlN or SiC), leading to a relatively quick growth of mixed AlN–SiC crystals at temperatures as low as 1800°C. Mixed AlN–SiC crystals vary in color from dark-blue to light-green. AlN–SiC alloys may also be useful as substrates for growth of AlN and GaN, and they exhibit interesting semiconductor properties. However, the material combinations 1 and 1a can not be considered as a promising way to grow semiconductor grade pure AlN.

The 'pure tungsten' furnance – another well-elaborated high-temperature heating system used in the arrangements 2 and 2a – includes two other challenges. First of all, the tungsten can be strongly attacked by aluminum vapor. This happens not only at high-temperatures as discussed in details in [1] but already at a temperature of about 1000°C and is caused by aluminum melt droplets, as partial decomposition of AlN occurs during pre-heating in vacuum. Hence the lifetime of tungsten heaters is relatively short. We have found that the W heater stability can be sufficiently improved by a precise furnace design and a proper heating regime, but the need of further corrections undoubtedly remains. Secondly, it is very difficult to remove inevitable oxygen (Al_2O_3 surface layer) from the AlN charge in a tungsten furnace. Annealing the powder mixture in $N_2 + H_2/NH_3$ at temperatures in the range of 1200–1500°C prior to growth is effective only for day-long reaction times. Growth in a W based furnace was always badly complicated by the formation of oxynitrides in the initial stage of growth. Seeded growth of AlN on SiC was very difficult to achieve as the seed quickly evaporates. This lead to the formation of greenish alloyed crystals of AlN–SiC in a similar way as in arrangement 1a. A change-over to growth of pure AlN was relatively smooth, but since monocrystallinity of the seed was usually destroyed already at the stage of alloy formation, only separate transparent light-yellow AlN crystals about 1 mm in size were grown as shown in Fig. 2. With the use of a W seeding plate, a dense and strongly adhering layer of AlN was formed. These layers are pale amber in appearance and built by well-developed prismatic crystals of 0.3–0.5 mm in diameter and up to 3 mm in length. X-ray powder analysis showed that they consist of pure wurzite AlN.

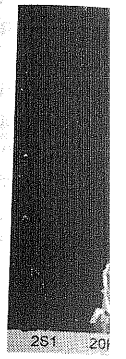

Fig. 2. A. AlN c
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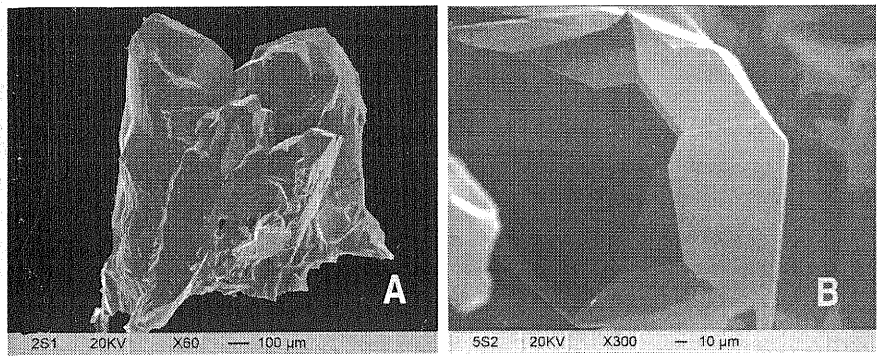

Fig. 2. A. AlN crystals grown in arrangement 2a. Growth time was 24 hours at 2100 C.
B. Well-formed end faces of an AlN prismatic crystal.

The combination of a W crucible and a graphite heater (arrangement 3) offers important advantages, such as long heater lifetime, effective use of the heating power and flexible cell design. A critical issue arising here is the probability of crucible damage because of WC formation on the outer surface. Furthermore, direct contact of tungsten with graphite parts has to be strictly avoided since the melting temperature of the W–WC eutectic is below 1900°C. However, it was found that in a properly designed system the erosion of the crucible is mainly determined by the action of aluminum vapor and not by carbon. Formation of oxynitrides was not observed. In arrangement 3 the best results of seeded AlN growth were achieved using SiC seeds. Layers up to 1 mm thick and 2–3 mm in size were grown after the transition stage of alloy formation. After growth the grown layer was always separated from the seed independent of the cooling rate. Cracking always occurred between the SiC bulk and the highly N-doped SiC surface layer, i.e. always within the seed itself and not through the grown layer.

Discussion. Since the only successful method for growing AlN was to employ a tungsten crucible, only the results of the experiments using arrangements 2, 2a and 3 will be discussed.

Crystal habit. AlN crystals grown under relatively stable conditions show mainly the {10$\underline{1}$0} and {10$\underline{1}$2} faces, see Fig. 2. The {0001} face was also sometimes present, but more often the rhombohedron end faces occurred. The best-formed, transparent crystals normally had a length to diameter ratio of about 3–5. Crystals of plate-like habit (typical for SiC Lely platelets) were not observed. This feature makes the use of spontaneously grown crystals for subsequent seeding more difficult.

AlN–SiC alloy crystals. Formation of AlN–SiC mixed crystals is an unavoidable step in seeded growth of AlN on SiC. Mixed crystals grown in our experimental conditions were variously colored from grayish-green to dark-blue. Shown in Fig. 3 are typical PL spectra detected for pure amber AlN and for dark-blue AlN-SiC crystals at room temperature. In PL measurements excitation was supplied by 309 or 363 nm lines an Ar+ ion laser. Comparison with the published literature data [3] for AlN crystals grown under different conditions points on the similarity of our material to the crystals grown by Campbell [4] using a high-temperature Lely vapor transport technique and a graphite crucible. This is surprising, since our arrangements were almost free from carbon (of course, carbon contamination from the SiC seed or graphite heater in 3 can not be excluded). In the SiC-AlN samples, PL of comparable intensity, but shifted

strongly to higher energy was observed. Despite of an evident presence of numerous luminescent centers in both crystals it is not possible to derive any specific chemical information from PL spectra, being in any case completely different for AlN and AlN-SiC.

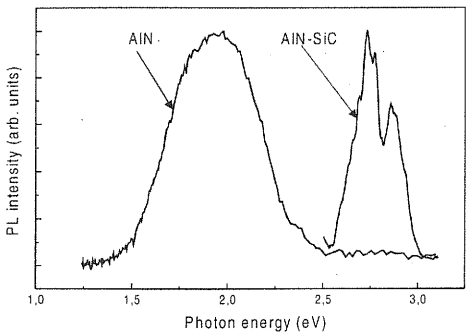

Fig. 3. PL emission spectra from pure AlN and from an AlN-SiC alloy under excitation at 309 nm and 363 nm correspondingly.

The alloyed intermediate layer can be useful for subsequent growth of pure AlN, since it allows smooth and continuous nucleation and helps to prevent cracking due to thermal coefficient mismatch [5]. However, practical realization of this transition is rather complicated at least within one growth process because of the strong difference in equilibrium pressures in the systems Al–N–Si–C and Al–N. Effective growth of AlN–SiC appears already at 1800°C, whereas the growth rate of pure AlN at 1800°C is only 3–5 μm/h. In order to enhance the growth rate up to 500 μm/h temperatures of 2200–2250°C are necessary as determined in our experiments with the W seed plate.

Mechanism of sublimation growth. Mechanism of AlN sublimation growth has been the subject of intensive discussions, see [6] and references within. It is generally believed that the small accommodation (sticking) coefficient of N_2 is responsible for the low growth rate of AlN. Our experimental observations on growth rate lead to a nonlinear dependence on nitrogen background pressure and were in qualitative agreement with the mechanism proposed in [4], but no difference was found between growth under pure N_2 ambient and growth in a $N_2 + NH_3$ gas mixture. The amount of active (dissociated) nitrogen has not a significant effect on the sublimation growth of AlN.

Conclusions. The best way of maintaining semiconductor-grade purity of the growing AlN crystal is the use of tungsten crucibles. However, further development of the AlN sublimation growth technique crucially depends on the development of a new growth unit configuration with improved purity and lifetime and on the development of a seeding procedure. The combination of tungsten crucible with graphite heating element and graphite isolation offers the most flexible design of the growth unit.

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