phys. stat. sol. (c) **4**, No. 7, 2281–2284 (2007) / **DOI** 10.1002/pssc.200674897

Growth of bulk aluminum nitride crystals

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Received 1 October 2006, revised 12 December 2006, accepted 14 December 2006
Published online 31 May 2007

PACS 81.10.Bk

We discuss the main growth issues for bulk AlN crystals: 1. durability of the crucible; 2. purity of the source; and 3. availability of large seeds. *In situ*-prepared TaC crucibles and re-crystallized powder sources are used in combination with SiC starting seeds to obtain high-quality AlN bulk single crystals.

1 Introduction Aluminum Nitride (AlN) is an important native substrate material for the growth of III-nitride epitaxy that does not occur naturally The first reported growth of bulk AlN by physical vapour transport (PVT) was by Slack and McNelly [1]. They grew AlN by self-seeding in tapered tungsten crucibles and found that the crucibles deteriorated rapidly. This work was dormant until about the mid-1990s when III-nitrides again gained prominence. Since then a number of groups have addressed PVT growth of AlN [2–4]. Essentially, three major problems with the growth of large bulk AlN crystals still remain: 1. the durability of the crucible; 2. the purity of the source of AlN; and 3. the availability of large seeds.

1.1 Durability of crucible In the physical vapour transport (PVT) growth of AlN aluminium vapour at the temperatures required for AlN growth is very corrosive. We have explored a number of crucible alternatives. In tungsten heated and insulated furnaces tungsten crucibles are highly durable provided that the concentration of other impurities is low with the AlN vapours. In graphite heated and insulated furnaces the carbo-nitride of tantalum is also durable. TaCN crucibles can also be used in the tungsten furnace; however, tungsten crucibles are not durable in a graphite environment. We have used both resistively and inductively heated graphite furnaces.

1.2 Purity of the source GDMS analysis shows that the primary impurity in AlN powder is oxygen. This is primarily due to the greater stability of the oxide than the nitride. Powder has a large surface area and the oxygen concentration can be considerable. We have reduced the oxygen concentration by re-crystallization of the powder.

1.3 Availability of seeds One objective of our program is to obtain 2” (50 mm) diameter substrates; however, AlN seeds of this diameter are not available. Indeed, when we began, AlN seeds were not available at all. We used SiC wafers as the initial seeds for the first small-diameter crystals. Rather than

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direct expansion of the seeds we have used large diameter SiC wafers as seeds and also mosaic seeds using oriented smaller wafers for larger crystals.

2 Solutions to problems

2.1 Crucible durability Currently our main production furnaces at Nitride Crystals are tungsten heated and insulated. The crucible used in these furnaces is W; however, seeds mounted on W or TaC plates are regularly used. The W crucibles and furnace are sensitive to contamination by Al vapour and by any residual Si in the seeds prepared on SiC wafers. The primary crucible material for seed preparation and growth of large diameter crystals is a patented, *in situ*-prepared tantalum carbo-nitride. Ta metal crucibles are converted into fully carbonized TaC crucibles in the graphite furnace. When fully carbonized these crucibles can be used also in the tungsten furnace.

Fig. 1 63 mm diameter TaC crucible converted *in situ* from Ta metal. The TaC is gold colour whereas Ta is dark grey.

When used to grow AlN the inside surface of the crucible converts to a carbo-nitride. If the Ta metal is not fully converted to the carbide, it will react with Al vapour to form a low-melting-point eutectic. Properly prepared TaCN crucibles are insensitive to impurities and have been used for over 3,000 hours of cumulative AlN growth without any remarkable change in the crucible properties in a small resistively heated graphite furnace. Large crucibles have been used in an inductively heated furnace for multiple hundred-hour runs. W crucibles, in the absence of deleterious impurities, have been used for several thousand hours in W furnaces.

2.2 Purity of the source We purify the AlN powder source material by re-crystallization. After re-crystallization the source is a deep orange to brown colour. GDMS analysis shows that the major impurity is still oxygen at approximately 10-100 ppm. The resulting crystals grown using the recrystallized source material are transparent and range in colour from yellow or orange to glass-clear.

UV transmission measurements show that crystals that are glass-clear can have deep UV transparency or a near UV cut-off. The crystal of Fig. 2 has a transmission cut-off at 320 nM. We do not currently understand the relative contributions of oxygen, native defects and other impurities to the transmission characteristics of the crystals.

Typical crystals have a multiple block structure with overall tilt and twist in the 300-600 arc sec range. Crystals such as the one of Fig. 2 show both tilt and twist that are in the 60-100 arc sec range. The measured dislocation density in this crystal is ~100/cm^2.

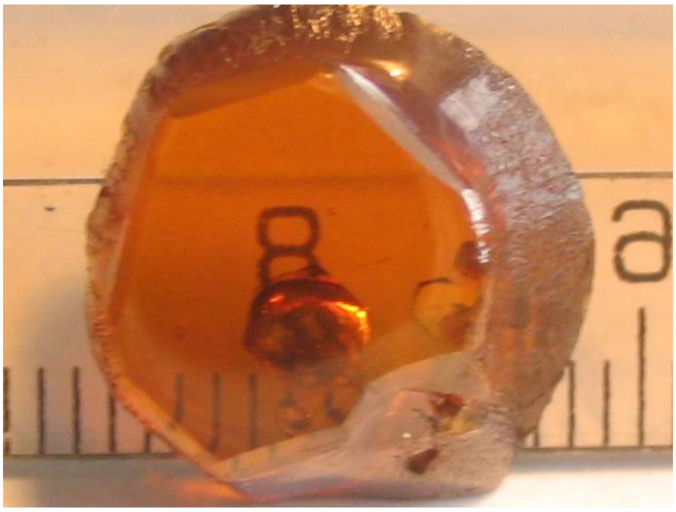

Fig. 2 12 mm diameter 12 mm long AlN single crystal grown with recrystallized source. Typical growth condition is 2150 °C at seed with growth rate of 100 µm/hr. Bragg FWHM ~ 90 arc sec.

2.3 Availability of seeds For our purposes, a key advantage of the TaC crucible is that it can be used to grow AlN on SiC seeds without any detrimental effects on the crucible. W crucibles cannot be used for growth on SiC seeds. Any residual Si damages the W crucible; therefore, the SiC is removed before the seed is used for further AlN growth. The cracks shown in Fig. 3 are completely eliminated in the growth after the seed is separated from the SiC initial seed. Presently we are working with 2” diameter SiC substrates as seed crystals to grow first 25-30 mm diameter AlN seed crystals and then 50 mm diameter crystals. To date we have grown up to 38 mm diameter AlN single crystals on SiC substrates.

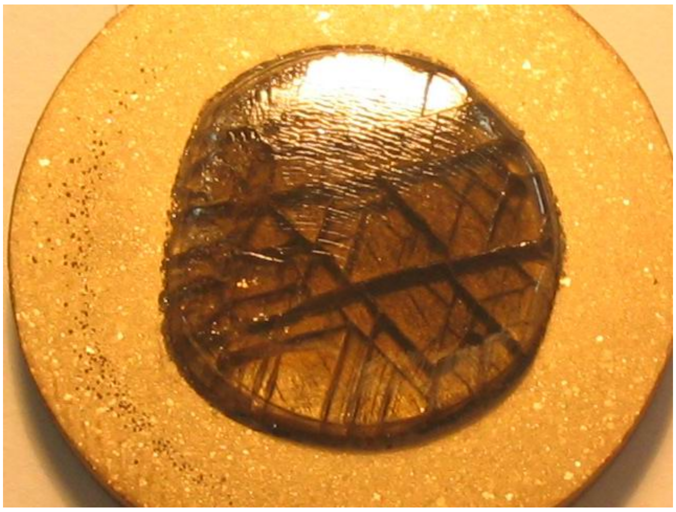

Fig. 3 Single crystal AlN seed grown on SiC starting seed. The SiC has been removed. Further AlN growth completely removes the cracks. Bragg FWHM ~ 60 arc sec.

3 Conclusions We have demonstrated that the *in situ*-prepared TaC crucibles are highly durable for the growth of large single crystal AlN crystals even using SiC as the seed substrate. Re-crystallization of AlN powder results in higher purity sources that can yield crystals with UV transmission down to 210 nM. Our continued activity is focused toward 2” diameter AlN substrates.

Acknowledgements Work by The Fox Group Inc was partially based on work supported by Naval Surface Warfare Centre, Dahlgren Division under Contract No.N00178-04-C-3105. Work at Nitride Crystals Ltd was partially supported by US CRDF Grant RS571.

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