Oxygen in PVT Growth of Bulk AlN: Influence on Growth Process and Crystal Properties.

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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 [1]. 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 [2]. 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 evaluate the influence of oxygen contamination in PVT growth of AlN on the crystal properties.

Sublimation experiments were performed with AlN powders containing up to 1 wt.% of Al_2O_3 in tungsten crucibles at temperatures in the range from 1200-2400°C. 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 and AlN particles at the early stage of growth (actually heating stage) because of oxygen assisted transport at low temperatures of 1500-1700°C. The temperature reversal method [3] where the seed was partially resublimed after bringing it to working temperature has been successfully used to avoid seed contamination.

We were able to fabricate AlN crystals with the lowest oxygen content reported up to date. Chemical analysis carried out by glow discharge mass spectroscopy (GDMS) showed an oxygen content of lower than 80 ppm wt, equaling a concentration of 1×10^{19} cm^{-3} in the crystal. Optical absorption measurements in the visible/near UV range reveal a broad absorption band. Following Slack and co-workers [4], it can be separated into two absorption bands. The first one in the range of 2.5 to 3.5 eV is attributed to nitrogen vacancies. The second one in the range 3.5 to 5.5 eV is reported to be linearly correlated to the oxygen content. The low absorption coefficient of $\alpha \approx 30$ cm^{-1} obtained in this range confirms the low oxygen content of our crystals. Thermal conductivities were measured by the laser flash method. High thermal conductivities of $\lambda = 186$ W / m K at room temperature also confirms that the concentration of aluminum vacancies introduced by oxygen contamination is in the low 10^{19} cm^{-3} range according to the phonon scattering model established by Slack et al. [4]. In the temperature range between 300 K and 1500 K, a $\lambda \propto T^{-1}$ dependence was found.

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