



In situ kinetic investigations during aluminium nitride purification and crystal growth processes by capillary coupled mass spectrometry

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ARTICLE INFO

Article history:

Received 17 June 2011

Received in revised form

14 September 2011

Accepted 21 September 2011

Available online 29 September 2011

Keywords:

AlN

Carbothermal reduction

Crystal growth

Purification processes

Kinetic analysis

Model-free analysis

Thermokinetics

ABSTRACT

Reaction models in the system Al–N–O–C–H are essential for intelligent purification of aluminium nitride source material and to predict time- and temperature-dependent reduction of oxygen-containing impurities. For several purposes, high purity AlN is needed; consequently it is an important goal to minimize the impurity values to a minimum possible prior to the single crystal growth. For these reasons in situ kinetic investigations with capillary coupled mass spectrometry were performed in the temperature range between 1160 °C and 2030 °C under streaming nitrogen at a pressure of 600 mbar. Conventional thermoanalytical methods like TG or DTA are not sensitive enough, signals overlay with AlN sublimation and the most commercially available systems strongly suffer from long measurement times ($t > 12$ h) at high temperatures.

Our custom built setup was optimized for a fast detection of evolved gases, for direct temperature measurement and for high temperature homogeneity of the powder sample up to 2050 °C. Kinetic parameters were calculated with model-free and model-based kinetic methods based on mass spectrometric data achieved by on-line process monitoring of gaseous species during the processes. This study highlights the usefulness of capillary coupled mass spectrometry in kinetic studies of carbothermal reduction processes. Predictions on basis of non-linear regression analyses of experimental MS data were performed.

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1. Introduction

The group III-nitride semiconductors play a leading role in today's opto-electronics. The AlGaInN system is of particular interest as it allows the realization of high efficiency light-emitting devices for the range from 400 nm up to 210 nm wavelength. Moreover, nitride-based semiconductors attract more and more attention regarding the utilization in very fast high power devices as well as high electron mobility transistors (HEMTs) for surface-acoustic-wave (SAW) and intersubband devices. Nevertheless, a drawback in nitride technology is given by the use of foreign substrates (sapphire or SiC) for active layer deposition. The device quality is suffering from high defect densities in the active layers generated by the structural misfit to the foreign substrate. Aluminium nitride may provide outstanding substrates, as it has closely matched lattice parameters and similar thermal properties. It is well known however that impurities like oxygen, carbon

and silicon can strongly affect the thermal, electric or optical properties of the material. For several purposes high purity is needed and consequently it is an important goal to minimize the impurity values to minimum ones before single crystal growth. Conventional strategies for powder purification are heating under high vacuum condition ($T < 1200$ °C), carbothermal reduction and nitridation by adding carbon to the powder ($T > 1500$ °C), sintering at high temperatures in nitrogen atmosphere ($T > 1900$ °C) or a total sublimation and condensation of the material ($T > 2100$ °C). In this paper we report on in situ and ex situ studies of different purification methods. Experiments were performed in a custom made setup, specially optimized for in situ kinetic investigation.

2. Background

Depending on processing route and storage of commercial aluminium nitride powders different solid phases occur as intrinsic impurities. In contact with atmospheric moisture AlN hydrolyses to amorphous AlOOH which further hydrolyses to mixtures of $\text{Al}(\text{OH})_3$ polymorphs namely bayerite, nordstrandite and gibbsite on AlN grain surfaces [1,2]. The hydrolyzed layer acts as a protection layer

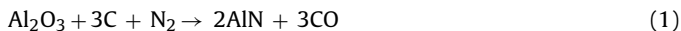
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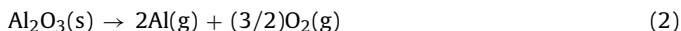
against further hydroxydation and oxidation of the powder. The surface areas of commercial powders are usually in the range of 1–8 m²/g which results in high values of aluminium hydroxides. If the processing route of the powder is based on carbothermal reduction and nitridation of alumina (starting from α -Al₂O₃ or γ -Al₂O₃) with carbon, residuals of α -Al₂O₃, C and small amounts of Al₂O₃C can appear beside the AlN main phase [3,4]. In literature, the appearance of AlON-phases as intermediate products during the production process is also discussed [5,6].

In the case of direct nitridation of aluminium as production method of the powder, aluminium hydroxides are the main impurities. Typical values for oxygen, carbon and hydrogen are in the range of 0.6–1.7 wt.%, 100–300 ppm and 70–200 ppm, respectively. Crystal growth starting from this impurity level would cause seed poisoning, growth of parasitic phases and a drastic degradation of the graphite based growth setup.

One of the methods which are commonly used as a first step for AlN purification is heating the powder at temperatures up to 1200 °C under high vacuum condition. The different hydroxides located at AlN surfaces undergo complex phase transitions during dehydration, rehydration and calcination in the temperature range of 150–1200 °C. The appearance of further Al(OH)₃ polymorphs like boehmite, transition aluminas (χ -, κ -, γ -, η -Al₂O₃), amorphous alumina and high temperature aluminas (δ -, θ -Al₂O₃) are possible during the process [7,8]. In the final stage starting between 1000 °C and 1045 °C the stable α -Al₂O₃ phase (corundum) is formed [9,10]. Until now little attention was paid to kinetic aspects of purification of aluminium nitride powder. Although well-investigated, the carbothermal reduction with simultaneous nitridation of alumina at $T > 1500$ °C, as one of the large-scale production methods for aluminium nitride powders, is still controversially discussed. Most authors [5,11,12] assume the overall reaction:



Lefort and Billy [5] postulated a kinetic model which describes the dissociation of alumina controlled by very low vapor pressure of oxygen in contact with carbon, followed by direct nitridation of aluminium according to:



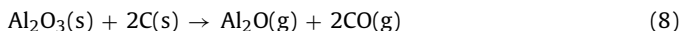
In this case the formation of carbon monoxide could also take place according to the following reactions:



immediately followed by



Some authors believe that the process proceeds via two steps. The different reaction pathways are summarized in the work of Forslund and Zheng [3]. They mention that the first step is the formation of Al(g) and Al₂O(g) in parallel reactions via:



which secondly react with nitrogen to AlN following reaction (4) and/or in additionally presence of carbon and/or CO to AlN via:

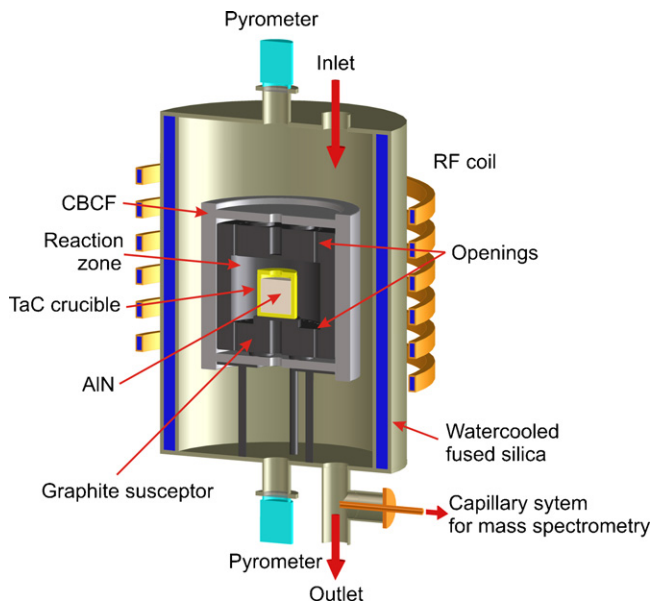
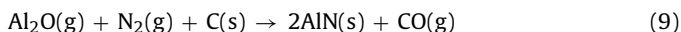


Fig. 1. Schematic sketch of the RF-heated apparatus for in situ kinetic investigations.

If CO₂ is present, it would further react to CO following Boudouard reaction (reaction (6)).

More recently Galvez et al. [13] studied the influence of different kinds of carbon on reaction rate and reaction extent. They applied the solid–solid diffusion model (s–s) as well as the gas–solid shrinking core (g–s) model. Significant deviations were determined which result in different activation energies E_A in the range of 356.8–815.3 kJ/mol of the reaction. Inorganic species containing Ca, K, Mg and transition metals like V, Fe, Ni could catalyze the formation of Al₂O(g) which is assumed to be the dominant species. Jung [14] studied γ -, δ - and α -Al₂O₃ in order to compare reactivities during carbothermal reduction and nitridation process. He found significant deviations in dependence on the studied phases, crystallinity and mixing homogeneity.

So far, a model for kinetic description of purification process of aluminium oxide containing aluminium nitride at high temperatures in nitrogen ambient was not found. Various reaction pathways of oxygen-including gaseous intermediate species like Al₂O, AlO, O₂, O are possible which finally end in CO(g) production by reactions with a carbon based furnace at high temperatures. The present work was undertaken in order to study the effect of different AlN purification methods in terms of their purification impact, and for a kinetic description of the processes. To the best of our knowledge it is the first time that in situ mass spectrometric methods were applied for kinetic analysis of carbothermal reduction processes. For the experimental investigations a home-made setup was designed for fast detection of evolved gases, for direct temperature measurement and for high temperature homogeneity of the sample up to 2050 °C.

3. Experimental

3.1. Apparatus

Experiments were carried out in a PID controlled RF-heated (10 kHz, 30 kW) glass chamber with a carbon based inset (Fig. 1). The custom made inset consists of high purity graphite (Ringsdorff CZ3P20) which works as susceptor and insulation parts made of carbon bonded carbon fiber (CBCF) for thermal insulation. Temperatures were measured close to the top and bottom of the TaC crucible by pyrometric method. Under streaming conditions

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