Journal of Crystal Growth 311 (2009) 3110–3113

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

In situ gravimetric monitoring of surface reactions between sapphire and NH_3

Kazuhiro Akiyama [a,*], Yasuhiro Ishii [a], Hisashi Murakami [b], Yoshinao Kumagai [b], Akinori Koukitu [b]

[a] *Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan*
[b] *Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan*

ARTICLE INFO

Available online 20 January 2009

PACS:
68.43.Vx
68.55.−a
68.60.Dv
81.05.Ea
81.65.Lp
82.30.Lp

Keywords:
A1. Surface processes
A1. Morphological stability
A3. Vapor-phase epitaxy
B1. Nitrides
B1. Sapphire
B2. Semiconducting aluminum compounds

ABSTRACT

Surface reactions between a (0 0 0 1) *C*-plane sapphire and NH_3, with He as an inert carrier gas, were investigated at high temperatures over 1200 °C using the *in situ* gravimetric monitoring method. Although the sapphire substrate was stable up to 1400 °C under a He atmosphere, decomposition started to occur at 1300 °C under a 0.1 atm NH_3+He and the decomposition rates were found to be lower than those in 0.1 atm H_2+He at each temperature. These results imply that sapphire can be decomposed by NH_3 and/or hydrogen generated by the decomposition of NH_3 over 1300 °C. The decomposition rate in NH_3+He was decreased with increase in NH_3 flow time, and the decomposition rate became constant after 60 min of NH_3 flow. Moreover, the activation energy for sapphire decomposition before 60 min of NH_3 flow was different from that after 60 min of NH_3 flow time, which indicates that the surface reaction between sapphire and NH_3 and/or hydrogen generated from NH_3 changes depending on the time of NH_3 flow. The dependence of the surface reactions and rate-limiting reactions between sapphire and NH_3 on the time of NH_3 flow is discussed.

1. Introduction

Sapphire is widely used as a substrate for the growth of AlN by vapor-phase epitaxy (VPE), including metalorganic VPE (MOVPE) and halogen-transport VPE (HVPE), due to its good thermal and chemical stability [1,2]. The growth of high-quality AlN requires a high growth temperature over 1200 °C. Several groups have attempted to grow high-quality AlN layers on (0 0 0 1) *C*-plane sapphire substrates at temperatures above 1200 °C by VPE [3–5]. Recently, high-quality AlN was fabricated over 1400 °C on a *C*-plane sapphire substrate [4–6]; however, little is known about the stability of *C*-plane sapphire substrates at such high temperatures. In our previous study, the thermal stability of sapphire and the reaction mechanisms between a sapphire surface and H_2 at high temperatures above 1200 °C were investigated using the *in situ* gravimetric monitoring (GM) system [7,8]. It was clarified that the sapphire surface is stable up to 1400 °C in flowing He at atmospheric pressure, and decomposition of the surface occurs at 1200 °C in flowing H_2.

On the other hand, NH_3 is used for the growth of AlN by VPE as a nitrogen source. The polarity of AlN is controlled by pre-growth treatment of the *C*-plane sapphire substrate in flowing NH_3 [9]. However, it is well known that H_2 is generated by the decomposition of NH_3 at high temperatures [10], and this H_2 is expected to react with the sapphire surface. Since NH_3 has a very important role in the growth of AlN on sapphire substrates by VPE above 1200 °C, the surface reaction between *C*-plane sapphire and NH_3, and the influence of H_2 generated by NH_3 decomposition on the decomposition of the sapphire substrate should be clarified. There have been a number of research studies on the surface morphology of sapphire exposed to NH_3, and X-ray photoelectron spectroscopic (XPS) studies of nitridation processes on the sapphire surface in NH_3 near 1000 °C [11–14]. Nonetheless, there have been few quantitative investigations of the surface reactions between sapphire and NH_3 at high temperature.

In this study, the reaction mechanisms between sapphire surface and NH_3 at high temperatures above 1200 °C were investigated using the *in situ* GM system [7,8]. This system is a powerful tool for investigating the surface reaction mechanisms, because it provides direct information on the decomposition rate due to the surface reaction in real time with a monolayer level.

2. Experimental procedure

The decomposition rate of the (0 0 0 1) *C*-plane sapphire in flowing NH_3 was monitored using the *in situ* GM system under atmospheric pressure at high temperatures. The GM apparatus

---

*Corresponding author. Tel.: +81 42 388 7035; fax: +81 42 386 3002.
E-mail address: aki-kazu@cc.tuat.ac.jp (K. Akiyama).

0022-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2009.01.079

consists of a vertical quartz glass reactor with a cold-wall heating system and a recording microbalance that provides direct information on the decomposition rate of the substrate, and detects dynamic weight changes with a sensitivity of 4 ng (ca. 1.7×10^{-6} μm in thickness of a 6.0 cm^2 area sapphire sample). The decomposition rate of sapphire was calculated on the weight change of the sapphire substrate monitored by the GM system and sapphire density to be 3.98 g/cm^3. A cylindrical graphite furnace, coated with pyrolytic boron nitride to prevent reaction between carbon and NH_3 at high temperatures, enables sample temperatures of over 1450 °C. A (0 0 0 1) *C*-plane sapphire substrate ($2.0\times1.5\times0.01$ cm^3) with both surfaces polished was used. The *C*-plane sapphire substrate was placed in the center of the cylindrical graphite furnace, which was suspended from the microbalance with a tungsten fiber and a fused quartz fiber in the high- and low-temperature zones of the reactor, respectively. He was used as the carrier gas. The decomposition rates of the *C*-plane sapphire substrate were measured in a flow of NH_3+He (the NH_3 partial pressure was 0.1 atm) at various temperatures.

Crystalline orientation and polarity of the nitrided layer formed on the *C*-plane sapphire exposed to flowing 0.1 atm NH_3+He were characterized by X-ray diffraction (XRD) (Spectris, X'Pert PRO MRD) and wet chemical etching in potassium hydroxide (KOH) solution, respectively. The thickness of the nitrided layer formed on the *C*-plane sapphire was observed by a scanning electron microscope (SEM) (JEOL, JSM-6700F).

3. Results and discussion

First, the decomposition rates of the *C*-plane sapphire at various temperatures were investigated. Fig. 1 shows a comparison of the decomposition rates in a flowing He [7], 0.1 atm NH_3+He, and 0.1 atm H_2+He. In a flowing He, the decomposition of sapphire was not observed below 1400 °C; however, a low rate of decomposition was observed above 1400 °C, which may be due to the direct desorption of Al, O_2, and AlO_x from the sapphire surface [7,8]. In the 0.1 atm NH_3+He flow, decomposition and/or reaction started to occur from 1300 °C, indicating that NH_3 significantly facilitates the surface reaction of *C*-plane sapphire. Moreover, it is seen that the decomposition rates in the 0.1 atm NH_3+He flow were lower than those in the 0.1 atm H_2 flow.

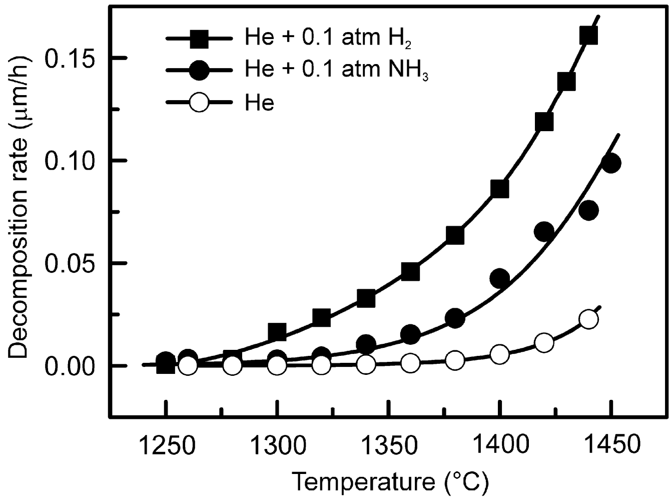

Fig. 1. Decomposition rates of *C*-plane sapphire in flowing He (open circles), 0.1 atm NH_3+He (solid circles), and 0.1 atm H_2+He (solid squares) for the temperature range from 1250 to 1450 °C.

It is reported that the duration of sapphire nitridation strongly affects the crystalline quality of AlN [15]. Therefore, the surface of the *C*-plane sapphire as a function of the NH_3 flow time was investigated. Fig. 2 shows the cross-sectional SEM micrographs of the *C*-plane sapphire after exposure to 0.1 atm NH_3 at 1440 °C, as a function of the NH_3 flow time. The thickness of the nitrided layer was found to increase with increase in NH_3 flow time up to 60 min, whereas the thickness was constant after 60 min of NH_3 flow time, which indicates completion of the *C*-plane sapphire nitridation at around 60 min in a 0.1 atm NH_3 flow at 1440 °C. This result is in agreement with another literature [14]. The nitrided layer formed on the *C*-plane sapphire exposed to flowing 0.1 atm NH_3+He at 1440 °C for 100 min was found to be N-polarity (0 0 0 1)AlN by XRD and wet chemical etching in KOH solution [16], and the in-plane orientation of the nitrided layer was found to be 30° rotated with respect to the *C*-plane sapphire as $[0\,0\,0\,1]_{AlN}\|[0\,0\,0\,1]_{sapphire}$ and $[1\,1\,\bar{2}\,0]_{AlN}\|[1\,0\,\bar{1}\,0]_{sapphire}$.

Fig. 3 shows the decomposition rates of the *C*-plane sapphire under 0.1 atm NH_3 flow plotted with an NH_3 flow time, along with the thickness of the nitrided layer as determined by SEM. Although the decomposition rates of the *C*-plane sapphire decreased as the NH_3 flow time increased up to 60 min, decomposition of the *C*-plane sapphire became constant after 60 min of NH_3 flow. This result is comparable to the saturation of the nitrided layer thickness after 60 min of NH_3 flow, and the dependence of the sapphire decomposition rate and the nitrided layer thickness on NH_3 flow time before 60 min fitted to a diffusion equation. However, the decomposition rate of sapphire is not zero even after 60 min of NH_3 flow, indicating some reactions on the sapphire still occur.

Fig. 4 shows the Arrhenius plots of the decomposition rates for the *C*-plane sapphire surface before and after 60 min of NH_3 flow time in the temperature range from 1380 to 1450 °C. The plotted decomposition rates before 60 min were decomposition rates on 0 min of NH_3 flow time obtained by fitting of a diffusion equation in decomposition rates depending on the NH_3 flow time at several temperatures (1380–1450 °C). Also, other Arrhenius plots on several NH_3 flow times before 60 min had approximately the same gradients. Different activation energies of 537 and 436 kJ/mol were obtained by exponential fitting of the decomposition rates before and after 60 min of NH_3 flow time, respectively. These results indicate a change in the reaction processes between the *C*-plane sapphire surface and NH_3 around 60 min of NH_3 exposure time.

The reactions occurring on the *C*-plane sapphire surface in flowing NH_3 are assumed to be as follows, according to a previous research [14]:

$$Al_2O_3\ (s) + 2NH_3\ (g) = 2AlN\ (s) + 3H_2O\ (g) \tag{1}$$

$$Al_2O_3\ (s) + (3+x)H_2\ (g) = 2AlH_x\ (g) + 3H_2O\ (g) \tag{2}$$

$$AlN\ (s) + ((3+y)/2)H_2\ (g) = AlH_y\ (g) + NH_3\ (g) \tag{3}$$

where *x* and *y* are 0 or 1. Reaction (1) represents the nitridation reaction between the sapphire and NH_3, including the diffusion of NH_3 through the AlN layer formed on the sapphire, and H_2O outward diffusion through the AlN layer [14]. Reaction (2) shows the sapphire decomposition reaction between sapphire (Al_2O_3) and H_2 generated by NH_3 decomposition, including the diffusion of H_2 through the AlN layer and also H_2O and AlH_x outward diffusions through the AlN layer [7,10,17]. Reaction (3) is the decomposition of the AlN layer in H_2 generated by NH_3 decomposition [18]. The decomposition rates before 60 min of NH_3 flow are dependent on the thickness of the nitrided layer