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Effects of AlN nucleation layers on the growth of AlN films using high temperature hydride vapor phase epitaxy

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ABSTRACT

AlN layers were grown on *c*-plane sapphire substrates with AlN nucleation layers (NLs) using high temperature hydride vapor phase epitaxy (HT-HVPE). Insertion of low temperature NLs, as those typically used in MOVPE process, prior to the high temperature AlN (HT-AlN) layers has been investigated. The NLs surface morphology was studied by atomic force microscopy (AFM) and NLs thickness was measured by X-ray reflectivity. Increasing nucleation layer deposition temperature from 650 to 850 °C has been found to promote the growth of c-oriented epitaxial HT-AlN layers instead of polycrystalline layers. The growth of polycrystalline layers has been related to the formation of dis-oriented crystallites. The density of such disoriented crystallites has been found to decrease while increasing NLs deposition temperature. The HT-AlN layers have been characterized by X-ray diffraction $\theta-2\theta$ scan and (0 0 0 2) rocking curve measurement, Raman and photoluminescence spectroscopies, AFM and field emission scanning electron microscopy. Increasing the growth temperature of HT-AlN layers from 1200 to 1400 °C using a NL grown at 850 °C improves the structural quality as well as the surface morphology. As a matter of fact, full-width at half-maximum (FWHM) of 0 0 0 2 reflections was improved from 1900 to 864 arcsec for 1200 °C and 1400 °C, respectively. Related RMS roughness also found to decrease from 10 to 5.6 nm.

1. Introduction

Aluminum nitride (AlN) single crystal is a promising substrate material for AlGaN based ultraviolet light emitting diodes (UV LEDs) [1], piezoelectric sensors [2], high-power and high temperature electronic devices [3,4] owing to its wide band gap (6.2 eV), high thermal conductivity (3.2 W cm^{-1} K^{-1}) and excellent lattice match with gallium nitride (GaN) [5,6]. AlN bulk single crystals grown by sublimation-recondensation and solution growth methods [7–10] are still limited by the size. Several techniques for growing aluminum nitride layers on a variety of substrates have been used, including molecular beam epitaxy (MBE) [11], metal-organic vapor phase epitaxy (MOVPE) [12] and hydride vapor phase epitaxy (HVPE) [13]. However thick AlN layers grown using HVPE or High Temperature Halide Chemical Vapor Deposition (HTCVD) [14] on sapphire (Al_2O_3) substrates have been widely considered as the alternative for the production of AlN substrates [15], due to the low cost and availability of Al_2O_3 in larger diameter. The large lattice mismatch between AlN and sapphire as well as poor Al adatom migration [12] makes high quality AlN growth on sapphire substrate more difficult than GaN neither by MOVPE nor by MBE. The initial growth stage plays a very important role in GaN and AlN epitaxial growth. The GaN epilayers with low-temperature AlN nucleation layers (NLs) have been vastly studied when compared to AlN epilayers grown on low temperature AlN NLs [16]. To achieve high growth rate, good surface morphology and crystalline quality,

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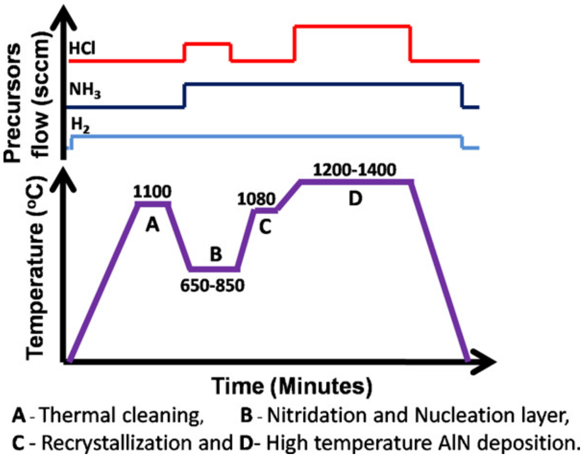

Fig. 1. HT-AlN Process temperatures and precursors flow *vs* time.

AlN deposition requires a high growth temperature above 1200 °C [14,17]. Nevertheless, thermal decomposition of c-plane sapphire starts to occur at 1200 °C [18] and AlN starts to decompose around 1400 °C [19] by reacting with hydrogen (H_2) used as a carrier gas, resulting in the formation of surface pits and in the degradation of AlN layer quality [20].

In this paper, the potential effect of using low temperature NLs for the growth of AlN layers by high temperature hydride vapor phase epitaxy (HT-HVPE) has been examined. The main idea is to grow AlN NLs at temperatures typically used in the case of AlN epitaxial growth by MOVPE [21,22] and higher than those used in the case of GaN epitaxial growth by MOVPE [23,24]. The significance of low temperature AlN NLs as well as deposition temperature of HT-AlN layers and its effects on surface morphology, structural and optical quality of AlN layers have been investigated.

2. Experimental procedure

AlN films were grown using HT-HVPE. The HT-HVPE setup consists of graphite susceptor heated by induction in a vertical water-cooled cold-wall reactor. The growth temperature was measured using a thermocouple inserted into the graphite susceptor [25]. Aluminium chloride ($AlCl_3$) and ammonia (NH_3) were used as the precursors for AlN deposition. $AlCl_3$ was formed through the *in situ* reaction between aluminium (Al) pellets and hydrogen chloride (HCl_g) at 500 °C. Hydrogen (H_2) was used as carrier gas. All the precursors used were 5 N (99.999%) grade purity. AlN growths were performed on 2″ c-plane sapphire epi-ready wafers. Sapphire substrate was loaded on graphite susceptor and thermally cleaned at 1100 °C for 10 min under H_2 ambient. Thermal cleaning was followed by nitridation, deposition of nucleation layers, recrystallization of NLs and growth of HT-AlN films.

To improve the quality of HT-AlN films, the NLs have been examined by varying deposition temperatures. The nucleation layer was deposited at 650, 750 and 850 °C on c-plane sapphire substrates. The as-grown NLs were first characterized then the same samples were reloaded into the reactor to perform high temperature (HT)-treatment. In order to study the characteristics of NLs prior to HT growth (without growing HT-AlN layers), the NLs were recrystallized at 1080 °C and further ramped up to 1200 °C (high temperature treatment) then cooled down under $H_2 + NH_3$ ambient. The NLs V/III flux ratio was kept constant at 30. The V/III ratio in the gas phase is calculated as the $NH_3/AlCl_3$ inlet flow rates ratio assuming that the chlorination reaction yield is equal to 1 and that $AlCl_3$ is the predominant $AlCl_x$ species [26]. The NLs were overgrown for 60 min to deposit high temperature (HT)-AlN layers. HT-AlN layers have been grown at 1200 °C directly on AlN nucleation layers after HT treatment (without air exposure). HT-AlN layers were grown in three groups, classified by the variation in nucleation layer deposition temperatures 650, 750 and 850 °C. Four HT-AlN samples have been grown in each NL deposition temperatures (650, 750 and 850 °C), all the 12 samples were grown with a V/III ratio of 10. Throughout all the growth steps, 2200 sccm of H_2 flow and 100 sccm of NH_3 flow were used and reactor pressure was maintained at 10 mbar (1300 Pa). Fig. 1 shows the growth steps of the HT-AlN layers.

The grown HT-AlN films with NLs deposited at different temperatures were structurally characterized by X-ray diffraction (XRD) using $\theta - 2\theta$ scan, rocking curve (XRC) of the (0 0 0 2) peak, Raman and photoluminescence (PL) spectroscopies. PL measurements were performed at low temperature (5 K) using an ArF-excimer laser emitting at 193 nm (6.42 eV). Surface morphology was accessed by tapping mode atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM). The RMS roughness was measured on 1 μm × 1 μm scan for NLs and 5 μm × 5 μm scan for HT-AlN samples. The average thickness of NLs and HT-AlN samples was measured by X-ray reflectivity (XRR) and cross sectional FE-SEM respectively. The thickness of all the HT-AlN samples was found to be approximately 2 μm. Finally, a comparison was made between the quality of HT-AlN films grown at 1200 and 1400 °C by employing optimal NLs process parameters.

3. Results and discussion

3.1. Low temperature nucleation layers

3.1.1. Surface morphology

The variation in surface morphology of NLs with respect to the deposition temperature is presented in Fig. 2. Fig. 2a and c shows the surface morphology of as-grown NLs at 650 and 850 °C. Fig. 2b and d depict the surface morphology of HT-treated NLs grown at 650 and 850 °C. The RMS roughness values for as-grown NLs at 650 °C (Fig. 2a) and HT-treated NLs (Fig. 2b) are found to be 3.5 nm and 2.5 nm respectively. The RMS roughness for as-grown NLs at 850 °C (Fig. 2c) and HT-treated NLs (Fig. 2d) are 1.3 nm and 1.0 nm, respectively. It is found that the RMS roughness decreases after HT-treatment, which is contradicting to AlN NLs grown using MOVPE [27]. The reduction in the RMS roughness values after the HT-treatment can be attributed to the rearrangement of nucleation islands (NIs) height. On the investigated surface under both deposition temperatures, the size of the NIs is found to vary and it can be distributed as small (<35 nm diameter and <4 nm height) and relatively big islands (>40 nm diameter and >5 nm height).

Table 1 presents the NIs density, size and height observed from the AFM images (Fig. 2). The nucleation islands density for all the nucleation layers is found to be in the order of $10^{11}\ cm^{-2}$. It is worth noting that the difference between small and big NIs densities is more pronounced at 850 °C. At both 650 and 850 °C, the increase of density for big NIs seems to explain the re-distribution process of NIs at high temperatures. However, lowest density of bigger NIs after HT-treatment has been observed at 850 °C NLs when compared with 650 °C NLs. There is almost no change in big NIs diameters after HT-treatment for 650 °C NLs. On other hand, noticeable increase has been observed in NIs diameter after HT-treatment for 850 °C NLs. The NIs height is decreased for both distributions after the HT-treatment of NLs grown at 650 °C whereas the height of both NIs distributions is found to remain unchanged for NLs grown at 850 °C.

Table 1
Nucleation islands (NIs) density, size and height observed from AFM images (Fig. 2).

NL deposition temperature (°C)	Conditions	NI density ($10^{10}\ cm^{-2}$)		NI diameter (nm)		NI height (nm)	
		Small	Big	Small	Big	Small	Big
650 (Fig. 2a)	As-grown	9	1	15–20	55–65	2–4	10–18
650 (Fig. 2b)	HT-treated	9	6	25–35	50–70	1–3	5–6
850 (Fig. 2c)	As-grown	8	0.08	15–21	40–45	2–3	5–9
850 (Fig. 2d)	HT-treated	10	0.2	20–30	50–75	2–4	5–9