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High temperature chemical vapor deposition of aluminum nitride, growth and evaluation

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ABSTRACT

The application of AlN films in optoelectronics, sensors and high temperature coatings is strongly dependent on the nano-micro-structure of the film, impurity level and defect density. AlN epitaxial thin (0.5–10 μm) and thick polycrystalline (>10 μm) films were grown on different foreign substrates (sapphire, silicon carbide, graphite) and single AlN crystals by Chemical Vapor Deposition (CVD), also called Hydride Vapor Phase Epitaxy (HVPE), at high temperature (1200–1750 °C). In the first part of this paper, polycrystalline growth of thick films (>10 μm) prepared at high growth rate (>100 $\mu m \cdot h^{-1}$) was performed on graphite substrates to study the preferential orientation of the films. AlN/W multilayers were deposited on silicon carbide composites to increase their performance at high temperature in aggressive conditions. Such multilayer materials can be used for the cladding of nuclear fuel. The second part of this paper concerns the characterization of epitaxial films, including their crystalline state, surface morphology, and inherent and thermally induced stress which inevitably leads to high defect densities and even cracking. The full-width at half-maximum (FWHM) of X-ray rocking curves of the grown AlN layers exhibited very large values (several thousand arcsec), and they became steeply deteriorated with increasing growth rate. To improve the crystalline quality of AlN layer, well-known growth techniques, such as multi-step growth using buffer layers, were used at temperatures above 1200 °C in order to lower the disorientation to 300 arcsec. The applications of such "templates" for deep UV light emitting diodes (UV LED) and surface acoustic wave sensors (SAW) are discussed.

1. Introduction

The chemical and physical properties of aluminum nitride have made it attractive for a wide range of applications in optoelectronics, including UV Light Emitting Diodes (UV LED) [1–3], thin film dielectrics, protective coatings [4,5], surface acoustic wave devices (SAW) [6,7] and high power electronics (High Electron Mobility Transistors) [8]. AlN is a good electrical insulator with a direct wide band gap of 6.2 eV. Moreover, it has a high decomposition temperature, good chemical stability, a thermal expansion coefficient (TEC) closely matched to that of others semiconductors as Si, SiC … (~4×10^{-6} K^{-1}), high thermal conductivity (~200 $W \cdot m^{-1} \cdot K^{-1}$), and a high electrical resistivity (~10^{11} $\Omega \cdot m$). The main processing achievement comes from the seeded sublimation physical vapor transport method where AlN powder is sublimated toward a seed at a low supersaturation. Recent results for this technique can be found in Ref. [9–12]. It was successfully developed by Slack and McNelly [13,14] in the mid-1970s. Several methods such as pulsed laser deposition (PLD) [15], chemical vapor deposition (CVD and MOCVD) [16] or hydride vapor phase epitaxy (HVPE) [17–20], molecular beam epitaxy (MBE) [21] and magnetron sputtering [22] have been employed for deposition of AlN thin or thick films for different applications. Important issues for deposition techniques [23–26] of the functional layers are: (1) large area deposition; (2) crystallinity of the grown layers; (3) residual stress and strain; (4) strain gradients in the multilayer architecture and (5) surface and interface morphology.

High temperature CVD (800–1800 °C) from chlorinated precursors and ammonia, $AlCl_3/NH_3$ diluted in N_2 and H_2, also called HVPE (Hydride Vapor Phase Epitaxy) is a common technique allowing the control of the microstructure as a function of temperature, nature of the gas-phase and nature of the substrate. This approach has been known for more than 50 years [27]. However, with new requirements of the performances of this material, control of defect density, orientation, doping, and microstructure, growth conditions, structural characterization and desired properties have to be re-evaluated and optimized. The processes have to be re-designed, the deposition temperatures increased and the upscaling of the reactors studied for the different applications.

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In this paper, the fabrication of mono- or polycrystalline AlN films (0.5 to 500 μm) is reviewed while keeping in mind different potential applications. We first studied the growth of thick films (>10 μm) at high growth rate (>100 $\mu m \cdot h^{-1}$) and at high temperature (>1500 °C) on graphite to analyze the preferential orientations of AlN films. The first application presented is more in the metallurgical side: the sealing of SiC/SiC composites which could be used in the cladding of fuel in nuclear reactor of generation IV. Very dense films stable at temperature higher than 1500 °C are required. The second study is the homo- and heteroepitaxial growth of thinner films (0.5–10 μm) on different single crystal substrates (sapphire, 6H-SiC and 2H-AlN). For deep UV LED application, a high crystalline quality of epitaxial layers is required: with FWHM less than 100 arcsec for the (0002) reflection. For piezoelectric sensors (SAW devices) the development of thick, crack-free and well-oriented (0001) films on sapphire or other foreign substrates is required with FWHM less than 5000 arcsec. The surface morphology and structural quality of the AlN layer are characterized by electron microscopy (FEG-SEM and TEM), Raman scattering spectroscopy, photoluminescence (PL) spectroscopy, atomic force microscopy (AFM), X-ray rocking curves (XRCs) and reflectivity (XRR). The impurity concentrations are measured by secondary ion mass spectrometry (SIMS). Chemical–mechanical polishing was used to prepare the surfaces before characterization [28,29].

2. Experimental procedure

The HT-HVPE set-up consists of a RF heated graphite susceptor in a vertical water-cooled cold-wall reactor (Fig. 1). The reactants used are ammonia NH_3 (99.999%) and aluminum chloride $AlCl_x$ species *in situ* formed via chlorination of high purity Al pellets (99.999%) with hydrogen chloride gas HCl or chlorine gas Cl_2 (99.999%) at 650 °C. H_2 (99.999%) is used as carrier gas. More details can be found in Ref. [30]. No gas purifiers were used in this set of experiments. The total pressure inside the reactor was set to 10 Torr (1333 Pa). The deposition temperature was measured inside the susceptor using a thermocouple or by an IR pyrometer.

For polycrystalline growth at high growth rate (>100 $\mu m \cdot h^{-1}$), the N/Al ratio in the gas phase was fixed to 3 in order to promote the growth of large-size grains. This N/Al ratio was 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 in these conditions [30]. The Cl_2 flow rate was fixed at a high value of 50 sccm in order to obtain a high growth rate (>100 $\mu m \cdot h^{-1}$). NH_3 and H_2 flow rates were 100 sccm (N/Al = 3) and 1000 sccm, respectively. These operating conditions lead to a high supersaturation in the gas phase that decreases with increasing temperature [30]. Typical deposition time varied from 1 to 3 h at temperatures higher than 1200 °C.

For epitaxial growth, "Epi-ready" 400 μm-thick on-axis (0001) sapphire, 6H-SiC and 2H-AlN single crystals were used as substrates for the fabrication of templates for UV LED and SAW devices. To improve the crystalline quality of high temperature films, low temperature nucleation layers were deposited at 850 °C on c-plane sapphire substrates (Fig. 1b) [31,32]. Thin AlN (0.5 to 5 μm) layers were directly grown at 1400 and 1500 °C on these nucleation layers.

Prior to deposition, a thermal cleaning under H_2 atmosphere was carried out at 1100 °C for 15 min. A 2 min pre-treatment with a low HCl flow rate (10 sccm) was performed at 1500 °C in order to saturate the substrate surface with Al species and to favor the Al-polar structure. After deposition, the ramp down to room temperature was achieved under NH_3 ambient in order to prevent the decomposition of AlN at high temperature.

The morphology of polycrystalline AlN layers was characterized by field emission scanning electron microscopy (FEG-SEM). Prior to XRD, Raman, and EBSD characterizations, some of the as-grown polycrystalline AlN layers were polished using a specific chemical mechanical polishing (CMP) process [28,29]. Surface morphology and roughness of thin films were studied by atomic force microscopy (AFM). The average thickness of thin nucleation layers was measured by X-ray reflectivity (XRR). The crystal structure and the orientation of the films were identified by electron backscattered diffraction (EBSD) and X-ray diffraction (XRD) rocking curves (ω-scans), using a 4-circle diffractometer and Cu Kα radiation (λ = 1.54 Å) of a rotating anode generator. Structural defects were shown using transmission electron microscopy (TEM). Crystalline structure and strain were characterized by Raman spectroscopy in backscattering geometry using an Ar^+ gas laser, at room temperature and by an optical profilometer (2.8 mm × 2.1 mm scan, with a lateral resolution of 3.8 μm and a vertical one of 0.1 nm). Light emission properties were accessed by photoluminescence (PL) spectroscopy. During PL measurements, samples were mounted in a He-flow cryostat allowing measurements at cryogenic temperatures down to 5 K. An excimer ArF* laser at 193 nm (6.4 eV) was used as a deep-UV excitation source, above the AlN bandgap energy (6.04 eV at 7 K).

3. Results

3.1. Polycrystalline thick coatings

The first deposition of polycrystalline AlN by CVD was performed by Renner and Anorg in 1959 [27], and most of the studies related

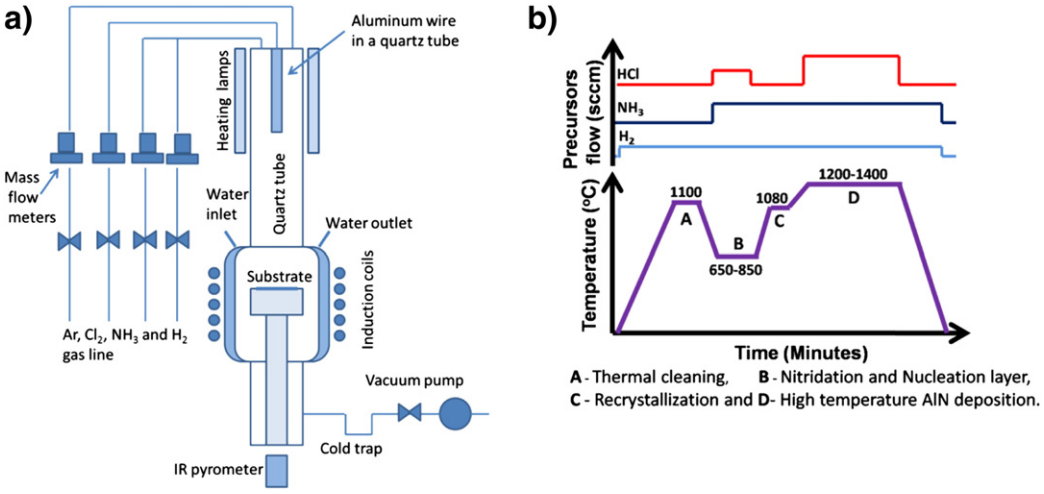

Fig. 1. (a) Schematic representation of the HT-HVPE reactor for AlN epitaxial growth and (b) process temperatures and precursors flow vs. time.