Preparation of the group III nitride thin films AlN, GaN, InN by direct and reactive pulsed laser ablation

Aldo Mele,[1,†] Anna Giardini,[1,2] Tonia M. Di Palma,[2] Chiara Flamini,[1]
Hideo Okabe,[3] and Roberto Teghil[4]

[1] *Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy*
[2] *CNR, Istituto Materiali Speciali, via S. Loja, 85050 Tito Scalo (PZ), Italy*
[3] *Material Science Research Center of Excellence, Howard University, Washington, DC 20059, USA*
[4] *Dipartimento di Chimica, Università della Basilicata, via N. Sauro, 85100 Potenza, Italy*

ABSTRACT. The methods of preparation of the group III nitrides AlN, GaN, and InN by laser ablation (i.e. laser sputtering), is here reviewed including studies on their properties. The technique, concerns direct ablation of nitride solid targets by laser to produce a plume which is collected on a substrate. Alternatively nitride deposition is obtained as a result of laser ablation of the metal and subsequent reaction in an NH_3 atmosphere. Optical multichannel emission spectroscopic analysis, and time of flight (TOF) mass spectrometry have been applied for *in situ* identification of deposition precursors in the plume moving from the target. Epitaxial AlN, GaN, and InN thin films on various substrates have been grown. X-ray diffraction, scanning electron microscopy, have been used to characterise thin films deposited by these methods.

1. INTRODUCTION

Research on thin-film deposition of AlN, GaN, and InN has been the subject of numerous review articles. The work concerns the various methods of preparation, and the recent impact on their applications in optics and microelectronics [1–3]. The importance of the group III nitrides AlN, GaN, and InN, which are wide-band semiconductors, is growing very fast because of the successful production of very intense light sources and detecting devices. The preparation of nitrides has been reported since at least 1928, and AlN, and GaN were in fact the first nitride semiconductors ever described [4–6]. Dingle *et al.* [7] observed a stimulated emission and laser action near 3.5 eV in single crystal needles of GaN, and they showed that laser action may be achieved near 3.44 eV. The electronic lighting technology has been very recently advanced with light-emitting diodes in the visible-infrared range and extended far into the ultraviolet (from 200 to 600 nm). These semiconductor devices show a very efficient electroluminescence (green to ultraviolet) when an electric current is passed through them. The real improvement in the field was represented by modulating the band-gap range from 1.89 eV for InN, to 3.4 eV for GaN, and to 6.2 eV for AlN by preparing thin films of their alloys [8–13]. Other properties of AlN, GaN and InN are reported on Table 1. Various authors [14–18] reported what is a very important step in the production of group III nitrides. It was based on the realization of current-injected laser diodes derived from a heterostructure composed of (In, Ga)N/GaN/(Al, Ga)N.

The relationship between bond length and band-gap energy as shown in Figure 1 serves as a basic consideration for device fabrication. It can be seen from Figure 1 that the systems AlN, GaN, and InN have E_g values from 1.89 eV to 3.39 eV, to 6.2 eV and chemical bond lengths from 2.16 Å to 1.95 Å to 1.90 Å. The latter values suggest that there could be good lattice matching conditions for a heterostructure between these nitrides.

Thin films of AlN, GaN, and InN have been grown by various methods which include metalorganic chemical vapor deposition (CVD) [19–23], microwave CVD [24],

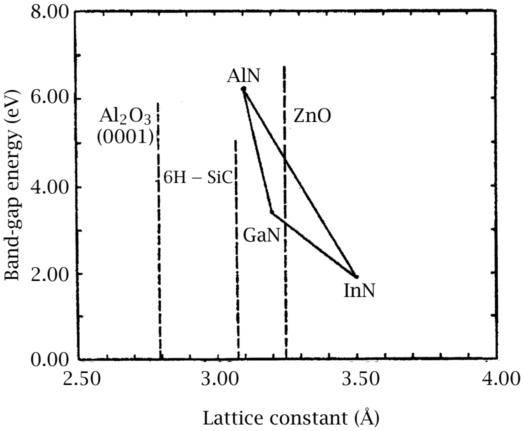

Figure 1. *Relationship between band-gap energy and lattice constant for* GaN, AlN, *and* InN. *The dashed lines refer to the lattice constant of a few candidate materials for substrates.*

[†] E-mail: aldo.mele@uniroma1.it

Table 1. Properties of wurtzite type nitrides (adapted from reference [1]).

	AlN	GaN	InN
Band gap Energy E_g (eV)	6.2	3.39	1.89
Band gap temperature coefficient (dE_g/dT) (eV/K) ($T > 180\,\mathrm{K}$)		-6.0×10^{-4}	-1.8×10^{-4}
Lattice constant (Å) ($T = 300\,\mathrm{K}$)	a = b =3.112 $c = 4.982$	a = b =3.189 $c = 5.185$	a= 3.548 $c = 5.76$
Bond strength(1) (eV)	11.53	8.591	7.08
Bond length(2) (nm)	0.1903	0.195	0.216
Coefficient of thermal expansion (K^{-1})($T = 300\,\mathrm{K}$)	$\Delta a/a = 4.2 \times 10^{-6}$ $\Delta c/c = 5.3 \times 10^{-6}$	$\Delta a/a = 4.2 \times 10^{-6}$ $\Delta c/c = 3.17 \times 10^{-6}$	
Thermal conductivity (W/cm K)	2	1.3	
Refractive index	2.15 ± 0.5	2.33	2.85
Dielectric constant	$\varepsilon_0 = 8.5 \pm 0.2$ $\varepsilon_\infty = 4.68$ $\varepsilon_\infty = 4.84$	$\varepsilon_0 = 8.9$ $\varepsilon_\infty = 5.35$	9.3(3)
Phonon modes ($T = 300\,\mathrm{K}$)	$TO = 667\,\mathrm{cm}^{-1}$ $E_2 = 665\,\mathrm{cm}^{-1}$ $LO = 910\,\mathrm{cm}^{-1}$	$A_1(TO) = 532\,\mathrm{cm}^{-1}$ $E_1(TO) = 560\,\mathrm{cm}^{-1}$ $E_2 = 144, 569\,\mathrm{cm}^{-1}$ $A_1(LO) = 710\,\mathrm{cm}^{-1}$ $E_1(TO) = 741\,\mathrm{cm}^{-1}$	$TO = 478\,\mathrm{cm}^{-1}$ $LO = 694\,\mathrm{cm}^{-1}$
Melting point (K)	> 2200	subl. 800	dec. 400
Bulk moduli (GPa)	202(4)	245(5)	165(6)
(*)Lattice mismatch to Si(100)	22.3	22.3	40

(1) From reference [95].
(2) From crystal structures.
(3) Landolt-Börnstrei (ed.), Numerical Data and Functional Relationships in Science Technology, New series, Vol. **17**, Springer-Verlag, Berlin, 1982.
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(5) P. Perlin, C. Jauberthie-Carillon, J. P. Itie, A. San Miguel, Phys. Rev B **45** (1992), 13307.
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(*) ($a_{\mathrm{epi}} - a_{\mathrm{sub}}/a_{\mathrm{sub}}$)% lattice constant along c axis.

electron cyclotron-resonance metalorganic molecular-beam epitaxy [25], CVD [26, 27], as well as combined laser and microwave plasma-enhanced CVD [28].

Laser ablation, is particularly well suited to grow thin films. In the last decade there have been many experimental and theoretical investigations of laser ablation (i.e. laser sputtering), especially for production of high-temperature superconducting films as well as semiconducting, insulating, ferroelectric, or other thin films [29–39].

A laser-assisted technique based on laser ablation of a group III element in the presence of ammonia has been found to be an active method to produce Al, Ga, and In nitride thin films [40]. The selective reaction between the gas-phase plume components from the Al, Ga, or In and the ammonia yields metal clusters and finally nitrides. The mechanism of conversion of metals and ammonia into nitrides controlling the chemical reaction is described in terms of the processes in the gas phase and on the target and substrate surface.

This review reports the growth of Al, Ga, and In nitride thin films by pulsed-laser ablation deposition either by direct ablation of nitride targets or by a reactive process by pulsed laser ablation and deposition of a metal target in the presence of gaseous ammonia. The information on the intermediates of the ablation (sputtering) process have been gathered from studies of the physics and chemistry of the gas phase during the deposition process. Plume emission spectroscopy was analyzed by an Optical Multichannel Analyzer (OMA). Mass spectra of the plume were measured by combining supersonic expansion with laser photoionization. The results of the film characterisation were obtained by conventional techniques such as X-ray diffraction (XRD), Rutterford Backscattering Spectroscopy (RBS), scanning electron microscopy (SEM), Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and energy dispersive X-ray analysis (EDX).

2. PLUME CHARACTERIZATION IN PLA

2.1. Optical spectroscopy. Neutral and ionised Al species are observed in the Optical Multichannel Ana-

Table 2. Surface electrical resistance of AlN obtained after laser irradiation at 1 atm, in air and in Ar + 4% H_2 [48].

Laser energy density (J/cm^2)	Surface resistance (Ω mm), Ar + 4% H_2	Surface resistance (Ω mm), air
1.0	∞	∞
1.5	60	65
2.0	30	32
3.0	25	30
5.0	25	25

lyzer (OMA) spectra of the gas cloud produced by Nd-YAG laser ablation of an Al target. Atomic Al (λ = 394.4–396.2 nm transition corresponding to $4s\,^2S \rightarrow 3p\,^2P^0$), and Al^{++} ions (λ = 451.2–452.9 nm transition corresponding to $4d\,^2D \rightarrow 4p\,^2P^0$) [28], are observed in the 0.5 nm resolution spectra. The results were confirmed together with a detailed analysis of the spatial and temporal distribution intensity line [41, 42]. Very intense peaks of excited states were also observed in the emission spectra of an Al and NH_3 mixture irradiated by a Nd-YAG laser. They were identified as not only excited state Al neutrals and ions but also as excited H and NH [43] We would suggest that an enhanced excitation on the front edge of the plume is produced by the NH_3 background, which causes a higher reactivity of the Al plume towards NH_3. Furthermore it has been found that the Al plume produced by a KrF laser in an ambient of 33 Pa NH_3 shows an emission peak (λ = 527.6 nm) which can be attributed to the AlN (1,0) band of the $A^3\Pi$-$X^3\Pi$ transition [44, 45] A band near 508 nm assignable to the AlN (0,0) band of the same transition has been observed from a mixture of Al and NH_3 irradiated by a Nd-YAG laser [46].

The OMA spectra of the In plume expanding in an NH_3 atmosphere reveal the presence of intense atomic and ionic In emission at λ = 451.1 nm, 465.6 nm, and 468.1 nm, as well as a weak emission at λ = 336.0 nm and 337.1 nm (NH $A^3\Pi$-$X^3\Sigma^-$ emission) and at λ = 433.9 nm, 486.1 nm, and 656.4 nm (hydrogen Lyman series) deriving from of NH_3 photodissociation [46].

2.2. Mass spectrometry. The species observed by time-resolved mass spectrometry of an AlN target irradiated by a Nd-YAG at λ = 1064 nm and with a fluence of 20 J/cm^2 are Al, N, AlN, N_2 as neutrals, and Al^+ as a positive ion [41–47]. The intensity ratio between aluminum and nitrogen indicates a larger depletion of nitrogen from the target. Post laser irradiation examination of the target surface reveals an aluminum metal coating consistent with the observed nitrogen deficiency in the plume. A similar result was obtained by Pedraza *et al.* [48] who used the laser technique to metallize aluminum nitride at the surface. The surface electrical resistance of an AlN target after laser irradiation is shown in Table 2.

Direct laser ablation and ionization by Laser Microprobe Mass Analysis (LAMMA) [41] of the plume from the same AlN target, as discussed above, showed the presence of Al^+ and N^+ ions. The ratio of Al^+ and N^+ is largely in favor of the former, thus confirming the results of the time-resolved mass spectra which do not show nitrogen ions at all.

Reactions of Al, Ga, and In in an NH_3 atmosphere were examined in a Smalley type vaporization system [49, 50]. In the case of a pure Al target typical sequences of $Al_n(NH_3)_m$ clusters are obtained by the reaction of the Al plume produced by laser ablation of an Al target with a mixture of NH_3 in He. Ablation by a KrF (λ = 248 nm) or by a Nd-YAG (λ = 532 nm) laser provides identical spectra. Similar experiments of laser ablation of Al and reaction with NH_3 in combination with supersonic expansion and laser-induced fluorescence (LIF) have been used to produce and detect AlN molecules [51, 52].

TOF mass spectra from the gas cloud obtained by laser ablation of pure Ga in a NH_3 atmosphere similarly show the presence of $Ga(NH_3)_n$ sequences [53]. TOF mass spectra of the species formed by reaction of In with NH_3 in the same molecular-beam apparatus show $In(NH_3)_n$ clusters [51]. The relative abundance of the large clusters increases by increasing the photon wavelength. Typical mass spectra of the clusters of group III elements and NH_3 are shown in Figure 2.

3. THIN-FILM PREPARATION

3.1. Direct pulsed laser ablation. Excimer laser (248 nm and 193 nm, 30 ns duration) ablation of sintered AlN powder has been used by Okabe *et al.* to grow thin films at room temperature on a variety of substrates [42]. Characterization of the films by various techniques such as FTIR, UV, and Auger spectroscopy has been accomplished. The FTIR trasmittance spectra were taken on an AlN film grown on KBr. The broad band between 500 and 900 cm^{-1} is due to the AlN phonon modes: LO at 737 cm^{-1}, TO_1 at 665 cm^{-1} and TO_2 at 630 cm^{-1}. The strong peaks of the phonon modes indicate that the composition of the film is mainly AlN. Raman spectroscopy was carried out by Vispute *et al.* [54, 55] using green light (514.5 nm line) from an Ar^+ ion laser on a polycrystalline AlN target and on an AlN film deposited on Si(111) at 750 °C. The

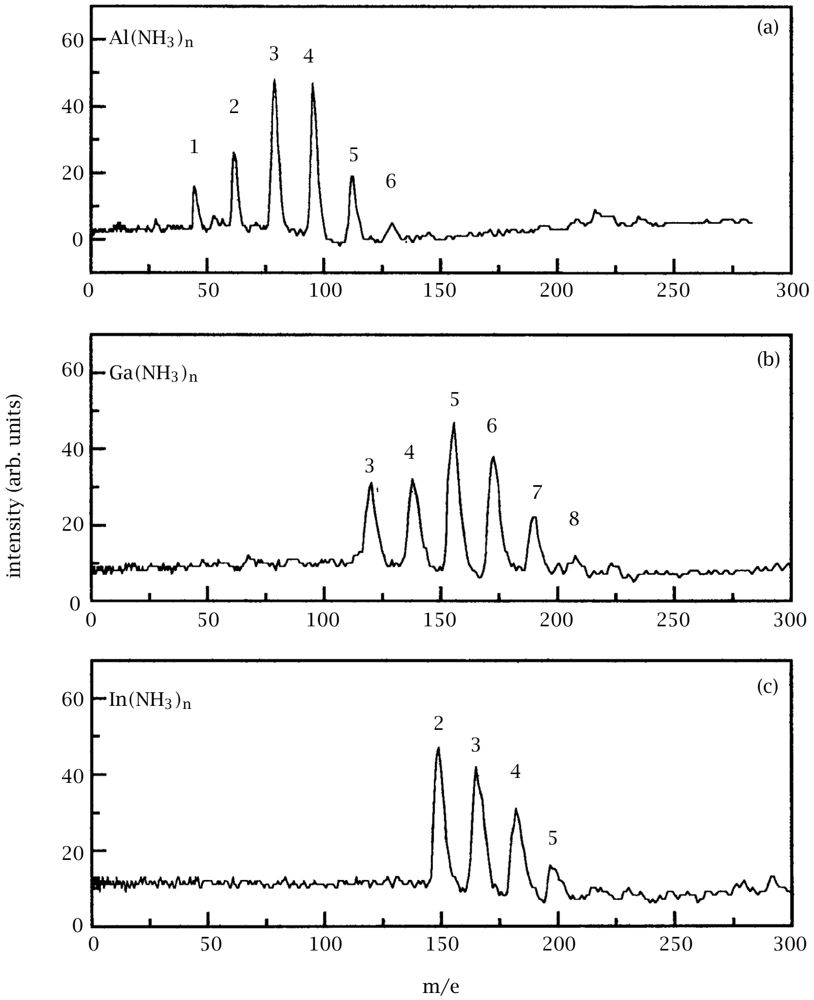


Figure 2. *Set of mass spectra of* $Al(NH_3)_n$, $Ga(NH_3)_n$, *and* $In(NH_3)_n$ *clusters by reaction of* Al, Ga, *and* In *plume in a stream of* NH_3 *and* He (10% He). *Stagnation pressure* 4×10^5 *Pa.* KrF *laser wavelength* 248 *nm. Laser fluence* 1 *J/cm*^{2}. *Ionization wavelength: (a)* 314 *nm, (b)* 315 *nm, (c)* 266 *nm [51].*

two spectra show the phonon mode with the frequencies in agreement with results reported above. These results clearly show that the laser deposited films contain pure AlN. The AlN band-gap was measured from the optical absorption spectra and results to be 6.15 eV in agreement with that of crystalline AlN (6.2 eV) [42, 55]. An Auger spectrum depth profile was obtained for an AlN film grown by laser ablation. The major constituents were Al and N, with no observable O atom inclusion [56].

Detailed X-ray diffraction measurements were carried out to study the crystalline properties of the laser deposited AlN film [55]. Figure 3 shows "Θ–2Θ" angular scans of the AlN films deposited on Si(111) at three different growth temperatures 550 °C, 650 °C, and 750 °C and a laser energy density of 3 J/cm^2, a pulse repetition rate of 15 Hz, and a base pressure of 4×10^{-5} Pa [55]. As can be seen from Figure 3 the diffraction patterns show the expected Si(111) family of planes together with AlN (0002) and AlN (0004) reflections. No other AlN reflection is present indicating that the AlN films deposited at all temperatures were predominantly oriented along the [0001] direction. The lattice constant c for these films was found to be 4.97 Å which is close to the literature value for bulk AlN. From Figure 3 it can be seen that the intensity of (0002) peak is low for the films deposited at 550 °C and increased as a function of temperature. The effect of the nitrogen partial pressure during laser deposition on the growth quality of AlN films was also investigated [55].

The results published [55] show that thin films of AlN can be grown epitaxially on Si(111) substrates by pulsed-laser ablation. The quality of the films was found to depend strongly on the laser fluence, substrate temperature, and nitrogen partial pressure. The electrical resistivity of films with thicknesses of

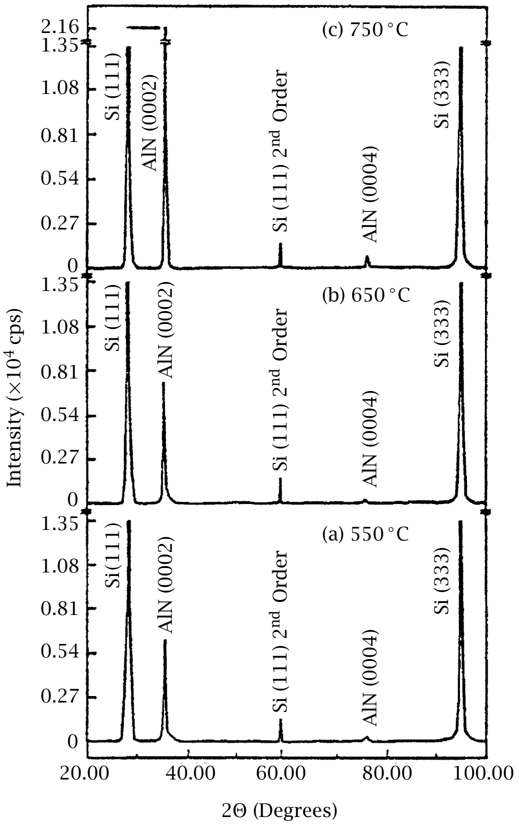


Figure 3. *X-ray diffraction patterns of laser deposited* AlN *films on* Si(111). *The* AlN *was deposited at a pressure of* 4×10^{-5} *Pa at three temperatures (a)* 550 °C, *(b)* 650 °C, *(c)* 750 °C *(*3 *J/cm*^{3}, 15 *Hz*, 10^{-5} *Pa) [55].*

0.2–0.3 μm was about 5 to 6×10^{13} ohms with a breakdown field of 5×10^6 V/cm. The growth rate was studied at fluences of 3 J/cm^2 and 10 J/cm^2. A value of 0.22 Å/pulse was found at 3 J/cm^2 and 1.12 Å/pulse at 10 J/cm^2. In the first case the film had a smooth surface, whereas at the higher fluence the film surface contained particulates.

The main difficulty with nitrides is the lack of suitable substrate material for film growth [1, 2]. The main parameters to account for a good matching between films and substrates are the structural and the thermal match, namely the lattice constants and the coefficients of thermal expansion. These should be similar. Group III nitrides have been grown on various substrates such as Al_2O_3 (sapphire), Si, SiC, MgO, and GaAs, despite the poor match with the nitrides. The lattice mismatch is usually defined as $(a_{\mathrm{epi}} - a_{\mathrm{sub}})/a_{\mathrm{sub}}(\%)$, where a is the lattice constant, “epi” refers to the epitaxial film, and “sub” refers to the substrate. The thermal expansion coefficients are evaluated similarly. It has been demonstrated that the epitaxial growth may be described also in terms of domain matching epitaxy $(ma_{\mathrm{epi}} - na_{\mathrm{sub}})/na_{\mathrm{sub}}(\%)$, where m and n are simple integers [55]. It is possible to overcome the lack of suitable substrates by fabrication of interlayers with a better match with the film. Epitaxial AlN films (100 nm thickness) were grown on epi-ZnO/sapphire. Single-crystal ZnO thin films with near perfect crystallinity have also been prepared by the PLA technique. The heterostructures with ZnO as well as 6H − SiC have excellent crystalline properties as lattice-matched substrates for group III nitride heteroepitaxial and optoelectronic devices [57]. As can be seen from Figure 1 ZnO is a good candidate for substrates for all three AlN, GaN, and InN. The hexagonal ZnO structure has lattice parameters $a = 3.252$ Å and $c = 5.213$ Å, and a band gap energy $E_g = 3.3$ eV. These fall nicely within the triangle, described by AlN, GaN, and InN.

Epitaxial GaN films with high crystalline quality and with thickness of 0.5–1.5 μm. have successfully grown directly on Al_2O_3 (0001) substrates at 950 °C by pulsed-laser ablation [58]. The crystalline quality of the GaN layers was evaluated using four-circle X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), and the ion channeling technique. ZnO thin films have been grown heteroepitaxially on epi-GaN/sapphire 0001 substrate with the aim to fabricate nitride optoelectronic devices. Low temperature cathodeluminescence studies also indicate high optical quality of these films presumably due to the close lattice match and stacking order between ZnO and GaN [59]. The X-ray diffraction and ion channeling measurements indicate near perfect alignment of the ZnO epilayers on GaN as compared to those grown directly on sapphire (0001).

Recently highly oriented AlN thin films were grown on sapphire (0001) substrate in a high vacuum 3×10^{-5} Pa by PLAD from an AlN target with a Kr excimer laser ($\lambda = 248$ nm, energy $= 350$ mJ, duration 30 nm fluence 3–5 J/cm^2) [60]. The experiment were performed with great accuracy in order to prevent contamination of the target and of the substarte. The films were produced at different temperature, laser energy and substrate temperature. Aluminum, Nitrogen, Oxygen and Carbon depth profile of a 250 nm thick of AlN film on sapphire was measured by Elastic Recoil Detection Analysis (ERDA). It was found that all films contains around 50 at % Aluminum, 42–49 at % of Nitrogen, and Oxygen was the difference to 99.5%. This result was confirmed by Rutterford Back Scattering (RBS). The AlN (0002) peak was the only non substrate peak appearing in the XRD spectra.

A recent paper reports a first attempt to grow AlN films by reactive laser ablation in an atmosphere of active nitrogen obtained by a RF discharge. The influence of nitrogen pressure on the composition and structure of the films has been studied. The main problem in AlN films growth was the oxygen incorporation [61].

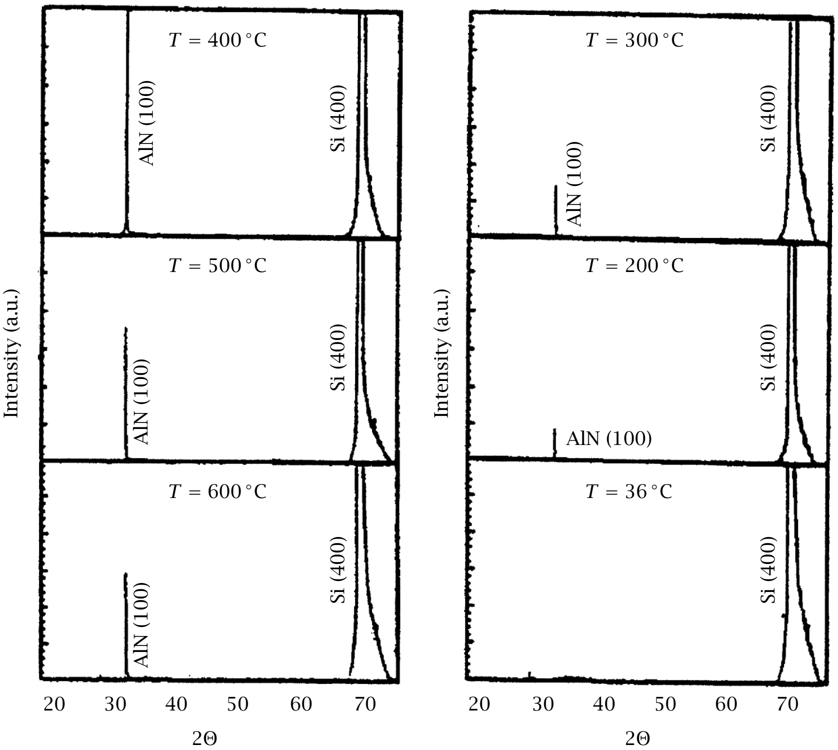


Figure 4. *X-ray diffraction patterns from* AlN *films grown on* Si (100) *at different substrate temperatures. The films were prepared from* Al *plume and* NH_3 *background at* 200 *Pa pressure, Nd-YAG laser (*$\lambda = 532$ *nm). Laser fluence* 6.5 *J/cm*^{2} *[63].*

3.2. Reactive pulsed-laser ablation and deposition. The growth of thin film of Al, Ga, and In nitrides by combining laser ablation of group III element and gaseous ammonia have been successfully exploited in the recent year [40, 53, 62]. The method can be viewed as a deposition process occurring by reaction of the laser generated plasma from a metal target with NH_3. It is suggested that the formation of nitrides may require at some stage of the process a strong interaction of the metal with atomic or other excited nitrogen containing species from NH_3 which are produced in quantities sufficient to form nitrides. The method has been applied to Ga [53], to Al [43, 53], and more recently also to In [62]. The gas-phase reaction between the metals and NH_3 has been found to produce metal-ammonia clusters as shown in a previous paragraph, and these products may likely have a role in the nitride formation.

Thin films of AlN were first produced by PLA method and the surface analysed by EDX spectra show the presence of Al and N. The ratio may be strictly stoichiometric depending on the experimental conditions. EDX spectra of films deposited on Si(100) and on Si(111) show peaks of Al and N as main components of the film on Si(100) with slight impurities of C and O. the film on Si(111) contains AlN and a significant amount of oxygen. Formation of AlN is confirmed by the transmittance IR spectrum of the film deposited on KBr [40, 64].

The X-ray diffraction spectra on Si(100) have been compared for different substrate temperatures and ammonia background pressures at the same fluence of 6.5 J/cm^2. XRD patterns showed diffraction primarily from 100 planes indicating that AlN is growing along the *a* axis, i.e. with the *b* and *c* axes parallel to the film-substrate interface plane Si(100). No crystalline deposit takes place on Si(111). The effect of the substrate temperature at 266 Pa NH_3 pressure is such that only at temperatures above 500–600 °C can a high degree of preferential orientation be observed [43, 63]. The trend of the spectra as a function of the substrate temperature in Figure 4 is similar to the films obtained by direct PLAD as reported in [55] for the growth on Si(111). This confirms that films of high crystalline quality are obtained preferentially at high temperature.

The NH_3 pressure has been varied between 25 Pa and 1000 Pa at the same substrate temperature of 600 °C and the same fluence of 6.5 J/cm^2. The XRD spectra show that the degree of the preferential orientation varies with the ammonia pressure. In Figure 5 the results for the AlN (100) preferential orientation have been summarized, and show an increase with the ammonia pressure up to about 230–250 Pa. Above this pressure the peak of AlN (100) at $2\theta = 33.2°$ scattering angle decreases [63].

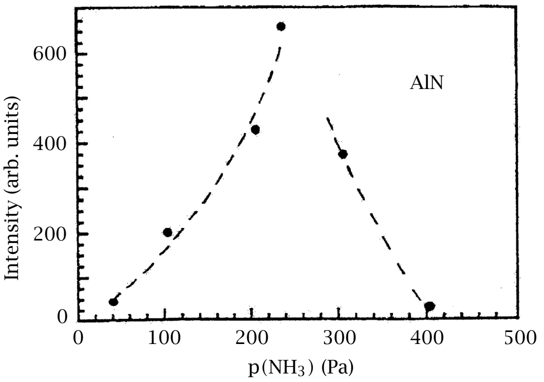
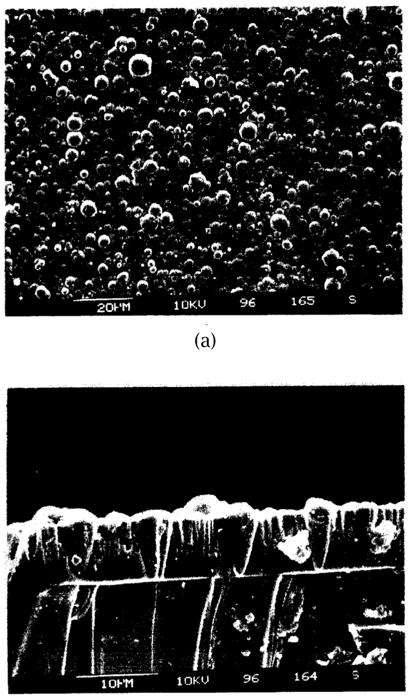


Figure 5. *The normalized XRD intensity of the* AlN *thin film* (100) *peak on* Si(100) *substrate at* 600 °*C at* $2\theta = 33.2°$ *scattering angle, plotted versus the* NH_3 *pressure [63].*



(a)

(b)

Figure 6. *SEM picture of* AlN *deposited on a* Si (100) *substrate at* 500 ° *C by reaction of an* Al *plume with* NH_3. *Laser wavelength* 532 *nm, laser fluence* 6.5 *J/cm*^{2}. *(a) surface pattern. (b) sectional microstructure [63].*

A scanning electron micrograph (SEM) of AlN grown on a Si crystal with (100) orientation shows a typical surface morphology as reported in Figure 6(a). The film shows a surface roughness which features the columnar growth of the crystal microstructure. The sectional micrograph of Figure 6(b) confirms a columnar texture. It has been found a dimensional correspondence of the two microstructures, namely surface and section [63]. The surface roughness, which has an average size between 0.5 and 4–5 μm, is the boundary of the columnar microstructure which is underneath. The sectional micrographs, (as in Figure 6(b)) show in some cases a non-rigorous cylindrical columnar texture. This seems to suggest that some anisotropy develops during the film growth.

Reactive PLAD has been accomplished also with Ga – NH_3 and GaAs – NH_3 [53]. TOF mass spectra derived from the gas cloud obtained by laser ablation of pure Ga or GaAs in an NH_3 atmosphere have shown the typical sequence of $Ga(NH_3)_n$ clusters with n from 1 to 9 as also found for other systems as mentioned previously (Figure 2) [51]. The formation of Ga – N bonds is confirmed by the trasmission IR spectra of the film deposited on Si. The IR spectra show a strong band in the region between 450 cm^{-1} to 800 cm^{-1} which may be attributed to a convolution of the GaN phonon modes $A_1(TO) = 532\,cm^{-1}$, $E_1(TO) = 560\,cm^{-1}$, $A_1(LO) = 710\,cm^{-1}$, and $E_1(TO) = 741\,cm^{-1}$ [53].

The X-ray diffraction (XRD) spectra of GaN films grown on a Si(100) substrate which are reported in Figure 7 indicate a high degree of preferential orientation with no other contributions. The spectra show a strong peak at $2\theta = 33.4$ corresponding to GaN(100) hexagonal wurtzite [53]. The substrate temperature seems to be an important factor for the crystallinity of the films (Figures 7(a) and 7(b)) for the PLA of bare Ga target. The best polycrystalline film was obtained around 200 °C, although a crystalline deposit is prepared also at room temperature. As seen in Figure 7(c) and 7(d), a crystalline film can also be fabricated by laser ablation of GaAs in NH_3. In these figures the XRD spectra of the hexagonal GaN is present together with unreacted deposit GaAs. This latter peak tends to disappear at a higher temperature. It is worth mentioning that GaN formation takes place also on the Ga target surface when the latter is irradiated in the presence of NH_3 [53].

Indium nitride films have also been produced by reaction of laser ablated In with NH_3 and deposition on a Si(100) substrate [62]. The analysis of mass spectra and of the films have confirmed that nitridation of the In plume by NH_3 produces $In(NH_3)_n$ clusters and at the end films of InN. X-ray diffraction spectra of the films grown on Si(100), show a high degree of preferential oriented growth on the (101) plane of the hexagonal wurtzite structure of InN. It has also been found that the best crystalline growth is obtained in the temperature range from 200 to 300 °C, at a laser fluence not higher than 6 J/cm^2. Similarly to AlN thin film deposition, the XRD peak intensity of InN reaches a maximum at $P(NH_3) = 266$ Pa at 4 J/cm^2 . SEM analysis indicates also for InN that the film is grown similar to AlN with a columnar structure. Different factors such as the high rate of deposition, low substrate temperature, and the presence of reactive buffer gas, all of which tend to de-

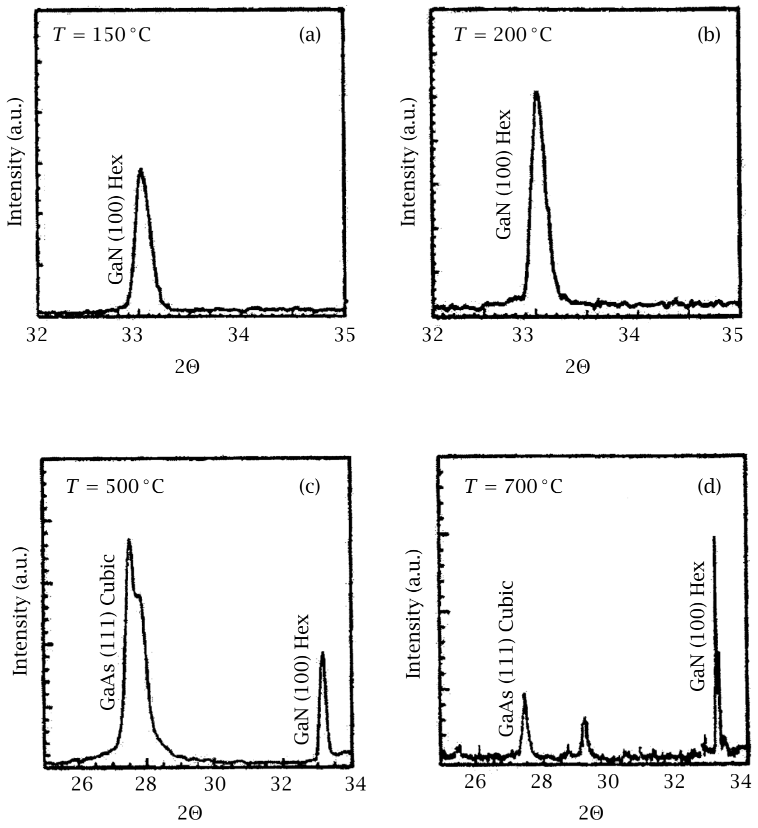


Figure 7. *XRD spectra of* GaN *thin film deposited by Nd-YAG laser* ($\lambda = 532$ *nm*) *at a fluence of* 6 *J/cm*^{2} *and at* 266 *Pa* NH_3. *(a) and (b) from* Ga *target; (c) and (d) from a* GaAs *target [53].*

crease the adatom mobility, may influence the formation of this columnar structure [43, 53, 62]. The EDX spectra of films formed on Si(100) show the presence of both In and N together with a certain amount of oxygen. The deposition rate at a fluence of 4 J/cm^2 was determined to be about 0.1 nm/pulse [43].

A mechanism of nitride formation is here suggested on the basis of the experimental results. Reaction between metals (Me) and NH_3 to yield nitrides may be viewed according to the following reaction scheme:

$$2Me + 2NH_3 \longrightarrow 2MeN + 3H_2 \text{ target,} \tag{1}$$

$$2Me + 2nNH_3 \longrightarrow 2Me(NH_3)_n \text{ gas phase,} \tag{2}$$

$$Me(NH_3)_n \longrightarrow nMeN + 3n/2H_2 \text{ substrate or gas phase,} \tag{3}$$

where reactions (1) and (2) assume direct formation of MeN on the target and $Me(NH_3)$ in the gas phase. In reaction (3) the hypothesis is that $Me(NH_3)$ clusters are the intermediates for the MeN deposition. Mass spectrometry provides clear evidence of the presence of $Me(NH_3)_n$ clusters in the gas phase as shown in equation (2) [51]. The binding energy of $Me - NH_3$ has been measured to be about 1 eV, for Al, Ga and $In - NH_3$ clusters [51] indicating a rather stable structure. The next step presumably takes place on the substrate surface where ($Me(NH_3)_n$) clusters are collected. These clusters are adsorbed on the Si (100) substrate surface through a dangling bond [65] as shown schematically in Figure 8. Finally the $N - H$ bonds dissociate thermally to yield the nitride according to equation (3). Detachment of molecular H_2 may be favored by adsorption of the clusters on the Si atom surface because of a substrate-mediated coupling of the $N - H$ vibration to the N-metal surface coordinates [66]. Equation (1) is a case of direct nitridation through thermal dissociation or photodissociation of NH_3. In addition the metal target surface may also yield MeN through equation (1).

GaN thin films with a wurtzite structure were grown on fused silica substrates also by PLAD of a liquid gallium target in the presence of gaseous NH_3. It has been found that single c-axis oriented GaN films can be formed if a thin (< 100 nm) ZnO buffer layer was first grown on a fresh substrate. The authors [67, 68] claim that the main advantage of liquid-target pulsed-laser deposition with respect to the use of a solid target is that the target will never deteriorate and that the formation of large particulates on the growing film can be completely prevented.

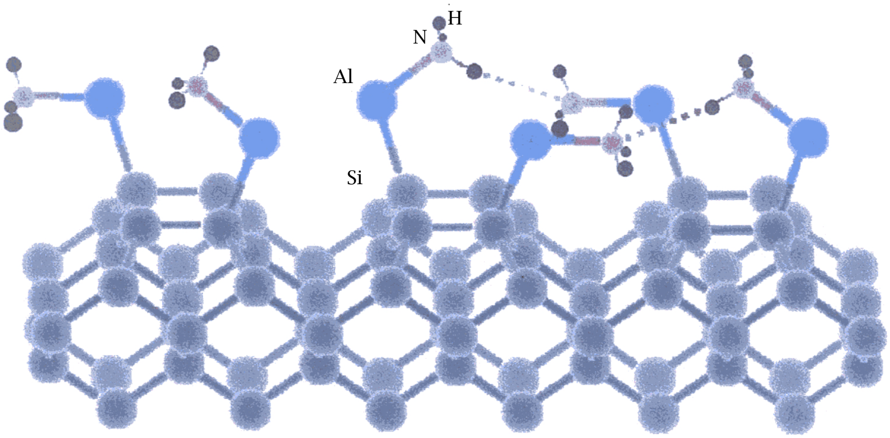


Figure 8. *Schematic of* $Me(NH_3)_n$ *clusters physically adsorbed on a* Si *(*100*) surface [53].*

4. CONCLUSIONS

Pulsed-laser deposition (PLD) in recent years has become a routine laboratory technique. Unfortunately there is a lack of standardization to make possible a comparison of the results obtained in various laboratories. This is probably one of the main problems to take into account if a production process has to be designed. This concerns nitride film production but also all the variety of compounds that have been treated by PLD. The study of the processes has shown that most parameters affecting the deposited film properties are interrelated [29–31].

This review treats mainly, but not exclusively, on work done by the authors. PLAD of third group nitride is an example of the application of the technique to the direct ablation and reactive ablation and concerns also general problems of PLA and specifics cases of deposition.

The work on the methods of thin film deposition is accompanied by an investigation of the effect of the process parameters such as target properties, laser fluence, gas pressure, temperature, and the characteristics of the substrate materials. There are several issues that need to be resolved. The large efforts on the subject provide strong support for the future, especially for the growth of a genuinely good material by PLD for commercial application. The many studies already carried out rarely report on the optical properties which are very important together with crystallinity and morphology. Nitrides prepared by laser ablation are interesting from the view point of achieving reliable light-emitting devices competitive with commercial products obtained by other methods [59].

The plume composition may be different from the target due to the nitrogen depletion. Supplemental nitrogen may be supplied by using N_2 or active N by RF as a background gas. The problem associated with the N_2 pressure in equilibrium with the metal is discussed extensively by Slack *et al.* [69] for AlN at various temperatures from thermodynamical data. Pulsed laser ablation is a process which depends strongly on the laser energy and laser-pulse duration [70]. These parameters affect the plume composition with respect to the target and finally also affect the deposit [71]. The influence of the plume velocity on the process depend on the energy density and there is an obvious effect on the growth rate, but there may also be an effect on the growth mode [32, 54].

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