Thermoluminescence of AlN. Influence of Synthesis Processes

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Received: December 19, 1994; In Final Form: March 21, 1995®

The behavior of excited centers due to oxygen impurities in the AlN lattice is reported for the first time by thermoluminescence (TL), studies between 77 and 550 K after 253.7 nm UV excitation. According to the origin of the product, the TL brings to the fore important differences due essentially to the synthesis process. The measurements of fluorescence let appear emission bands around 3.2 eV identified as due to substitutional oxygen and a very narrow one at 2.1 eV characteristic of Mn^{4+} ions observed before by EPR measurements. At last, measurements of FTIR confirm, as supposed from TL, the presence of γ-AlON in one of the studied samples even if it is under the form of marks only.

Introduction

Aluminum nitride (AlN) crystallizes in the hexagonal system and has a large gap around 5.85 eV with a direct transition.[1-3] AlN is characterized by a blue-violet luminescence, sometimes called "self-activated". This emission is generally attributed to the oxygen impurities introduced in the AlN lattice during the preparation process,[1,4] the storage, and the aging. This phenomenon is due to the high chemical affinity existing between aluminum and oxygen.

Besides its high thermal conductivity (200–210 W/(m·K) at 300 K), close to that of metals, the AlN is an excellent electrical insulator; at 300 K, its electrical resistivity ϱ is greater than 10^{12} Ω·m.[5] Due to these very interesting qualities, the aluminum nitride seems to be an ideal material for several applications in microelectronics, where the phenomenon of thermal dissipation is a major problem. As seen in the past ten years on the market and by the amount of patents registered,[6] aluminum nitride is an excellent candidate for a substrate for power hybrid circuits or like radiators in electronic assembling, preceeding materials used until now such as alumina (Al_2O_3) or silicon carbide (SiC). Let us cite beryllium oxide (BeO), which would be an excellent candidate if it was not toxic.

The research of the behavior of the oxygen impurity in the AlN lattice is important to understand the process of luminescence in this component. Three AlN samples called A, B, and C of various origins have been studied by thermoluminescence (TL). This technique allows us to define some trapping centers, responsible for the observed signals in TL, and the luminescence centers, responsible for the emission of these peaks.

Experimental Conditions

1. Thermoluminescence (TL). A small quantity (about 2 mg) of AlN powder is dropped on an aluminum cupel of diameter 9 mm by the acetone sedimentation technique. The sample is excited with a UV low-pressure mercury lamp working at a wavelength of $\lambda = 254$ nm (4.89 eV). The temperature of the excitation is −196 °C. The heating occurs at a rate of 30 °C/min under a secondary vacuum of 2.7×10^{-3} Pa to 300 °C. The excitation duration is 5 min. The detection of the thermoluminescence is realized with two RTC photomultipliers, the "2018 B" with S13 photocathode, between 200

TABLE 1

studied sample	Δn (m³)	c (nm)
A	6.593×10^{26}	0.498 016
B	4.853×10^{26}	0.498 054
C	6.090×10^{26}	0.498 027

and 600 nm, and the "XP 1017" with S20R photocathode, between 300 and 850 nm. The TL spectral distribution is made between 250 and 850 nm with interferential filters with a transmission of 30–50% and a band half-width of about 15 nm. The curves obtained are corrected according to the response of the photomultiplier and filter passbands.

2. Fluorescence. The emission spectrum is recorded between 250 and 700 nm thanks to an H 25 grating monochromator of Jobin-Yvon connected to a R 928 Hamamatsu photomultiplier, associated to a picoammeter and a drawing table. The excitation is effective at 300 K with the help of a xenon lamp shown through a second H 25 grating monochromator associated to interferential filters. The excitation spectrum is realized with a high-pass filtration ($\lambda < 300$ nm) to eliminate any excitation trace in modifying the excitation wavelength from 200 to 500 nm.

3. Spectrophotometry. The spectra of diffuse reflectance are done with the help of a CARY 5E spectrophotometer with a sphere of integration of diameter 110 mm at room temperature from 250 to 2500 nm.

Crystallochemical Properties of Aluminum Nitride

In order to elaborate the study, we first report in Table 1 the number (Δn) of nitrogen atoms replaced by those of oxygen in our samples as well as the values of the corresponding unit cell parameter c, obtained according to the relation mentioned below and according to which the AlN lattice constant decreases with increasing oxygen concentration:[7]

$$\frac{\Delta c}{c_0} = -0.021 \frac{\Delta n}{n_0}$$

where $\Delta c = c - c_0$ with $c_0 = 0.498\ 16$ nm, the value of the parameter c in the case of pure AlN, and $n_0 = 4.79 \times 10^{28}$, the number of nitrogen atoms per cubic meter in pure AlN.

The unit cell of AlN is shown in Figure 1. Each aluminum atom (Al) is at the center of a tetrahedron in which the tops are occupied by nitrogen atoms (N) with which it engages four covalency bonds. The substitution of three nitrogen atoms (N_1,
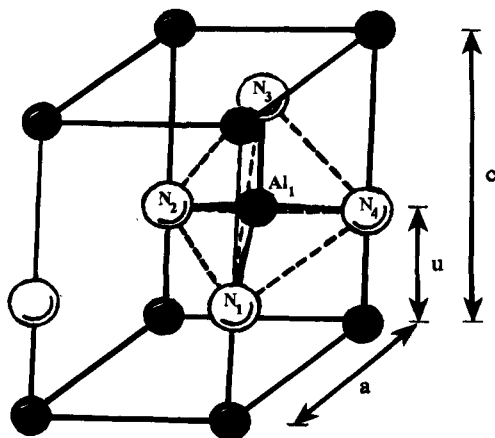
Figure 1. Modified unit cell of aluminum nitride according to J. P. Sachet.[7]

TABLE 2

| studied AlN sample	specific area B.E.T. (m^2/g)	Φ B.E.T. (μm)	granulometry		chemical analysis (%)			
			Φ_{max} (μm)	Φ_{50} (μm)	Al	N	O	C
A	4.4	0.42	25	4	64.8	33.3	2.2	0.5
B	2.4	0.77	5	2.1	65.5	33	1.1	<0.1
C	3.5	0.52	5	1.5	66	33.8	0.6	0.04

N_2, and N_3 for instance) by three oxygen atoms favors the apparition of an Al vacancy (Al_1). The unit cell parameters of aluminum nitride containing 2% oxygen by weight are $c = 0.4896$ nm and $a = 0.3114$ nm,[5] which correspond to $c/a = 1.572$.

In the following, the studied nitrides were fabricated according to two procedures well used in the industry: direct nitruration and classical carbonitruration. (a) Sample A is a result of direct nitruration[8] following the reaction

$$Al + \frac{1}{2}N_2 \rightarrow AlN$$
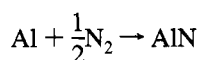
This reaction has to happen around 600 °C because fusion of the aluminum occurs at 660 °C. This method leads to particles with a granulometry of 20 μm, which are usually crushed (5 μm) to increase the reactivity of sintering. This is a major problem because the crushing always brings a risk of contamination of the product.

(b) Samples B and C are obtained by the classical technique of carbonitruration.[9] It leads to an AlN powder purer than the one obtained by a direct nitruration and with better properties of sintering. In this process, one starts with a homogeneous pulverulent mixing of alumina and carbon. The reduction of alumina by nitrogen is summarized by

$$Al_2O_3(s) + (3+x)C(s) + N_2(g) \rightarrow 3CO + 2AlN + xC(s)$$
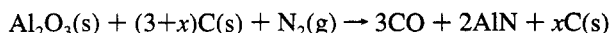
This reaction happens at temperatures lower than 1700 °C in order to avoid the formation of γ-AlON. It is followed by a treatment in a natural environment at about 650 °C in order to eliminate the carbon. At the end, we obtain a powder of the size lower than about 1 μm and of a gray color, due very probably to the presence of carbon impurities. We report in Table 2 some physical and chemical properties of the three studied AlN powders.[10]

Results

1. Thermoluminescence. *1.1. Curves.* We show in Figure 2 the TL curves obtained after 254 nm UV excitation between
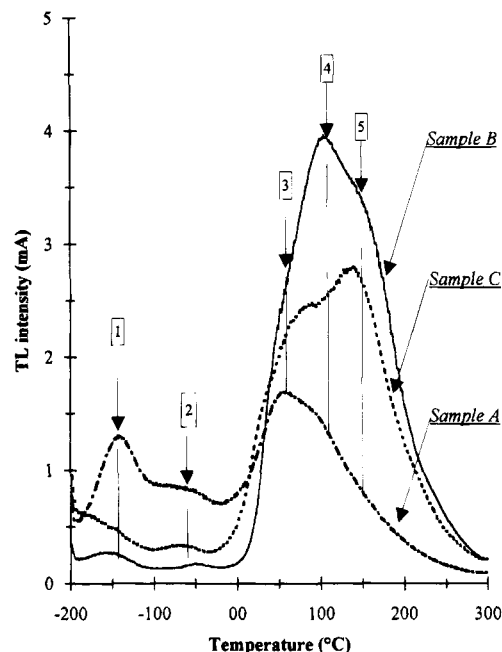

Figure 2. TL curves obtained on the three AlN samples after 254 nm UV excitation at 77 K for 5 min. Peaks 1, 2, 3, 4, and 5 are situated at respectively −150, −60, 60, 110, and 150 °C.

−196 and 300 °C on the three samples with a very good reproducibility of measurements.[11] We notice that, according to the origin of the product, important variations of TL intensities appear: the glow curves. We think that the curves are the result of superposition of at least five TL peaks which are located at the same temperatures (−140, −60, 60, 110, and 150 °C) for the different samples but which have variable relative intensities from one sample to the other. Next, we shall mainly look to the area of temperature included between 0 and 300 °C (peaks 3−5), where the intensity of the TL signal is predominantly found on every sample. Let us notice that, after X irradiation (45 kV, 3 Gy), no TL signal has been observed.

1.2. Thermoluminescence Spectral Analysis. Figure 3 represents the spectral repartition of the main TL peaks (3, 4, and 5, respectively) obtained from samples A, B, and C. For all samples, the emission centers are mainly characterized by a wide band centered around 3.3 eV with a shoulder at 3.7 eV. Only sample A also includes a narrower band at around 2 eV.

2. Fluorescence. *2.1. Emission Spectra.* Figure 4 shows spectra of an emission obtained at room temperature on the three AlN powders in the case of a 260 nm UV excitation (4.77 eV). The three spectra have in common a wide band centered around 3.1−3.2 eV and structured with several maxima (3.56, 3.16, 2.96, and 2.70 eV). We notice a shift of this band toward high energies when one goes from nitride A to nitride C and then B. Furthermore, as in TL, one observes on sample A another band of emission at 2.11 eV.

2.2. Excitation Spectra. No significant excitation band was ever noticed on our samples. This led us to conduct measurements of diffuse reflectance spectra (see next paragraph).

3. Spectrophotometry. Figure 5 represents the spectra of absorption deduced from the measurements of diffuse reflectance on the three AlN between 250 and 800 nm. For the three products, one notices a strong increase of absorption starting at 300 nm. For sample A, on which we observe the strongest absorption, two maxima seem to appear: one around 266 nm (4.66 eV) as well as another one around 370 nm (3.35 eV). Samples B and C have a weaker absorption, and no significant maximum was detected.
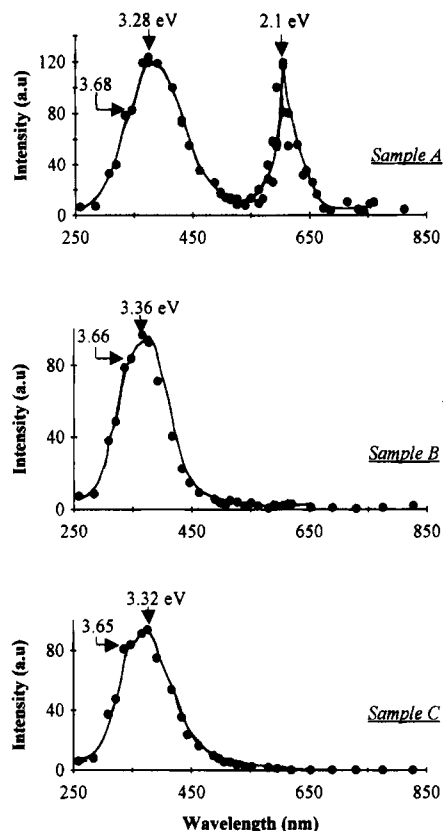
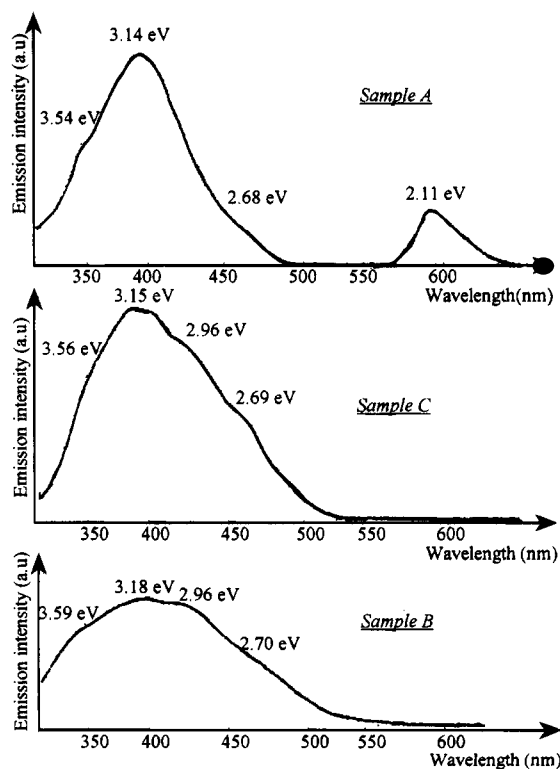**Figure 3.** Spectral repartition of the main TL peaks 3, 4, and 5 respectively situated at 60, 110, and 150 °C.

Figure 4. Emission spectra obtained at room temperature under 260 nm excitation.

4. XRD and FTIR Measurements. *4.1. XRD.* By X-ray diffraction at room temperature we notice that the diffraction line of the AlON cannot be found neither in the A sample's diffractogram nor in the B sample's one taken as reference. This points out that, within the limit of detection of this particular
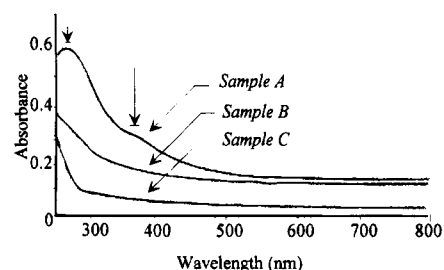

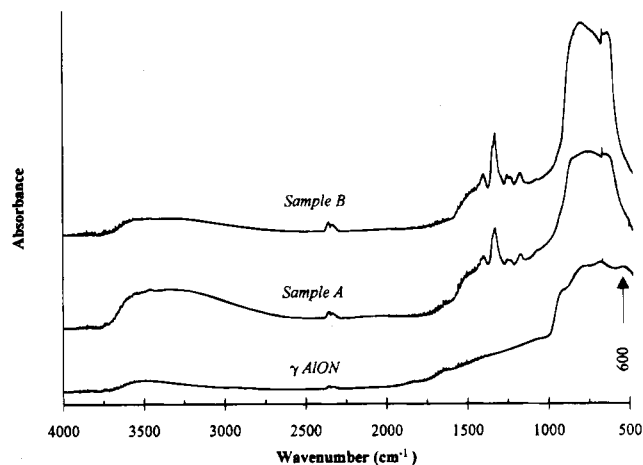**Figure 5.** Diffuse reflectance spectra observed on the three AlN samples at room temperature.

Figure 6. FTIR analysis of γ-AlON and AlN powders. The AlN curves are similar to those published by other authors.[12] The broad intense band at 600−900 cm⁻¹ corresponds to stretching vibrations of the Al−N bond. The group of bands around 1330 cm⁻¹ is typical to AlN.

method (around 1/1000), we cannot detect any presence of crystallized AlON.

4.2. FTIR. The FTIR analysis allows us to differentiate the AlON spectrum from the ones of the A and B AlN powders thanks to the presence of an absorption band around 600 cm⁻¹ (Figure 6). However we notice that a 600 cm⁻¹ shoulder is likely to be on the absorption band at 750 cm⁻¹ from the A sample.

Discussion

The TL emission (Figure 3) and fluorescence spectra are in agreement with the luminescence measurements reported in the literature,[13] which show that the spectrum of undoped AlN is a large band centered around 3.1−3.3 eV. This wide emission band common to all three studied samples shifts toward weak energies when the oxygen concentration increases and may be attributed to the characteristic emission of oxygen. In fact (1) in the case of samples B and C issued from the carbonitruration, the oxygen traces could be present under the form of α alumina, which would not react during the preparation process, under the form of AlON, due to the oxidation of the AlN, in substitution of N, creating then an aluminum vacancy V_{Al}, under the form of Al_2OC microdomains,[14] or on the surface, under the form of amorphous, crystallized, or hydrated alumina. (2) on the other hand, sample A, which is issued from the direct nitruration, should not normally contain any oxygen traces; nevertheless, it could be introduced during the crushing as previously mentioned in the Crystallochemical Properties section.

The very narrow band in which the maximum is at 2.1 eV and which is particular to sample A has already been noticed by Karel et al.[15,16] in fluorescence on AlN−Mn. It has been
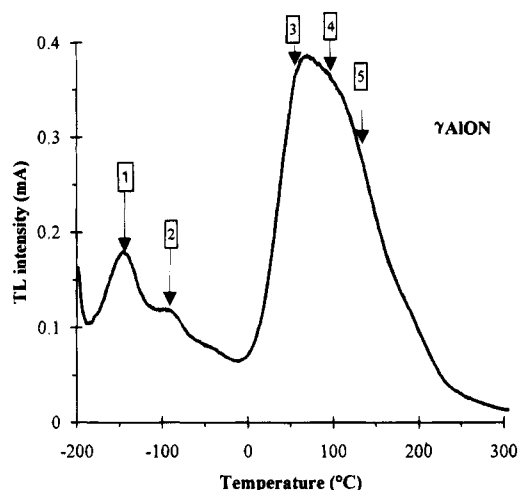
Figure 7. TL curve of γ-AlON after 254 nm UV excitation at 77 K for 5 min.

attributed to manganese ions which would substitute themselves for aluminum ions and would correspond to the transition $4T_2 \rightarrow 4T_1$. Such a transition would be possible if the manganese in the AlN lattice was under the form Mn^{4+}.[15] An analysis of our sample A in X fluorescence allows us to discover the presence of manganese of about 4 ppm.

In the precise case of aluminum nitride, the TL reveals the part played by the oxygen in the formation of trap levels (O_N) in the AlN lattice by substitution in the N sites.[13] The charge excess which is a direct result of it is compensated by the simultaneous formation of aluminum vacancies (V_{Al}).

According to Rosa et al.,[4] the association of the two types of defects V_{Al} and O_N probably forms complex centers denoted $V_{Al}-O_N$, which act as hole traps while the O_N centers, making the decisive part of impurities in AlN, play the role of electron traps. The mechanism of substitution of the nitrogen by the oxygen which leads to the creation of vacant aluminum sites has been studied.[17]

Some lines before, we mentioned that the oxygen may also be found under the form of Al_2O_3 or AlON. The TL curves of Al_2O_3 are well-known[18] and do not correspond to the ones we obtained on AlN. On the other hand, we focused our attention on the thermoluminescence signal of γ-AlON (Figure 7), which is very similar to that of sample A (Figure 2) but with a lower intensity. This similarity taken into account, we have decided to check if sample A contained some AlON. The presence of γ-AlON in sample A seems possible, but this is difficult to prove categorically because of the few differences noticed by X-ray diffraction and FTIR measurements.

Now, let us analyze the spectra of the fluorescence (Figure 4). According to the concentrations and the c unit cell parameter of each of the three given samples (Table 1), we notice, like in TL, that the maximum of the emission moves itself toward higher energies not only when the oxygen concentration in the AlN lattice decreases (3.14 eV for sample A, 3.15 eV for C, and finally 3.18 eV for B), according to ref 1, but also when the c unit cell parameter increases. This band around (3.16 ± 0.02) eV is predominant in all three studied nitrides.

The structuration of this wide fluorescence band may be connected to different oxygen impurity centers in the AlN lattice. The shoulder around (3.56 ± 0.03) eV seems to correspond to the band obtained by Pastrnak et al.[1] at (3.51 ± 0.03) eV, which is attributed to transitions from V_{Al} to O_N. The predominant band around (3.16 ± 0.02) eV could be attributed to a center $V_{Al}-O_N-3N$ where O_N is in the first anion coordination sphere.[1] The shoulder at 2.96 eV has already been observed[1] and has

been attributed to a center $V_{Al}-O_N-3N$ where O_N is this time in the second coordination sphere of the anion. Finally, the center $V_{Al}-2O_N-2N$, where the two O_N's are in the nearest anion coordination sphere,[1] may be responsible for the band at (2.69 ± 0.01) eV. As for the band of emission around 2.11 eV, particular to sample A, observed in fluorescence as well as in TL (Figure 3), it could be due to the presence (4 ppm) of manganese ions under the form Mn^{4+} and not Mn^{2+}, since the ionic radius of the Mn^{4+} ion is approximately equal to that of the Al^{3+} ion, whereas the one of Mn^{2+} is roughly double that. This result has already been confirmed by other authors[19] with the help of EPR measurements.

As for the two absorption maxima around 266 nm (4.66 eV) and 370 nm (3.35 eV), only observed for sample A, they could be either due to the presence of Mn, in comparison to the two other samples where there is a lack of an emission band at 2.11 eV attributed to Mn^{4+}, or due to oxygen vacancies more numerous in sample A than in samples B and C.

Conclusion

Besides the measurements of emission and excitation spectra already done by several authors, we have enriched the AlN study with a series of new measurements. First, the thermoluminescence allows us to distinguish the synthesis process of our products. This technique has also brought to the fore the presence of oxygen, which forms the main AlN impurity as well as the one of the manganese linked to the A sample. Then these differences have been confirmed by measurements of spectrophotometry where we can see two absorption bands from the A sample. Last, infrared spectra by Fourier transformation seem to confirm the thermoluminescence measurements where the A sample seems to contain some AlON, even if it is only marks.

Additional measurements of thermostimulated exoelectronic emission (TSEE) are planned in order to quantify the different rates of oxygen uptake in AlN and to see if AlON and Al_2O_3 would eventually be on the surface.

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