CONTROLLING THE PROPERTIES OF EPITAXIALLY GROWN OPTOELECTRONIC MATERIAL $Al_xGa_{1-x}N$ BY MODULATING THE STOICHIOMETRY

E. P. Koltsakis[1], H. M. Polatoglou[2]
Physics Dept, Aristotle University of Thessaloniki, Thessaloniki GR 54124, Greece

Abstract

$Al_xGa_{1-x}N$ alloys have been under investigation over the past few years, due to their potential for optoelectronic applications in the Visible and UV part of the spectrum, as wide gap semiconductors, high temperature electronics and blue diodes. Recently, long-range atomic ordering (LRAO) has been discovered in AlGaN and InGaN alloys. The study of growth phenomena, which lead to an understanding of ordering, is important since one expects ordering to influence the optical and electronic properties of these alloys. In the present work we analyze via modeling the relation between different $Al_xGa_{1-x}N$ ordering possibilities and the XRD patterns, and we discuss the experimental results, in order to understand the nature of the observed ordering.

Introduction

Devices that employ $Al_xGa_{1-x}N$ layers have recently been fabricated and include light emitting diodes, laser diodes, UV detectors etc[1-3]. The reported studies on the growth and characterization of these alloys are limited and their properties are not yet well understood.

LRAO has been discovered in AlGaN and InGaN alloys (III–V alloy semiconductors), grown by both molecular beam epitaxy (MBE)[4] and metalorganic chemical vapor deposition (MOCVD). In contrast with the cubic III–V arsenides and phosphides where ordering was previously observed[7-10], the $Al_xGa_{1-x}N$ system has the hexagonal wurtzite structure. Ordering in these alloys occurs along the (0001) closed packed planes during growth in the [0001] direction. This is contrary to what has been reported in cubic III–V alloys where ordering occurs in the closed packed (111) planes during growth in the [100] direction.

As it is determined by experiment, LRAO in AlGaN occurs along the [0001] direction while (0001) planes are disordered. Three periods of 2, 7 & 12 monolayers (ML) have been observed[4-6]; therefore there is some sort of stoichiometry modulation. In addition only the Ga sublattice is disordered. The ordered regions are embedded in a random matrix.

The aim of our study is to develop parametric models for $Al_xGa_{1-x}N$ super cells, where we could at will change the stoichiometry and the type of LRAO. We have produced a database of different types of LRAO and different stoichiometries. In addition, the X-Ray Diffraction (XRD) patterns for each case were created. The XRD pattern dependence and sensitivity, due to Al percentage and distribution, have been systematically studied and compared to the known experimental results.

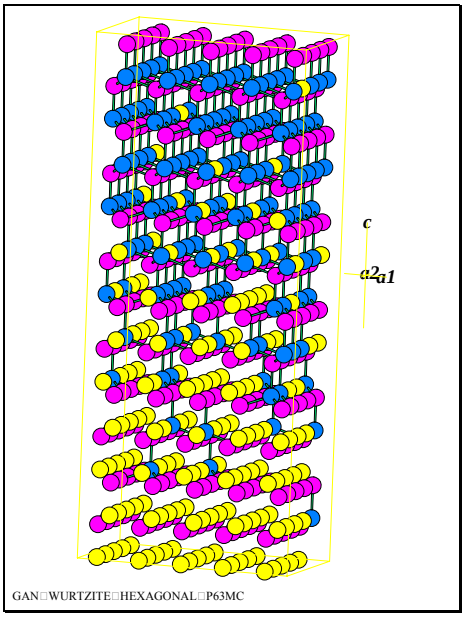

Fig. 1: 12 monolayer super cell

[1] *Contact e-mail: vangelis@auth.gr*
[2] *Contact e-mail: hariton@auth.gr*

Method

We need to build models with given periodicity along the [0001] direction and large enough along (0001) planes for the reproduction of in-plane disorder as can be seen in Fig. 1. We found that 25 atomic positions in each plane, randomly occupied by Ga or Al atoms were enough to avoid the interference with the ordering along the [0001] direction.

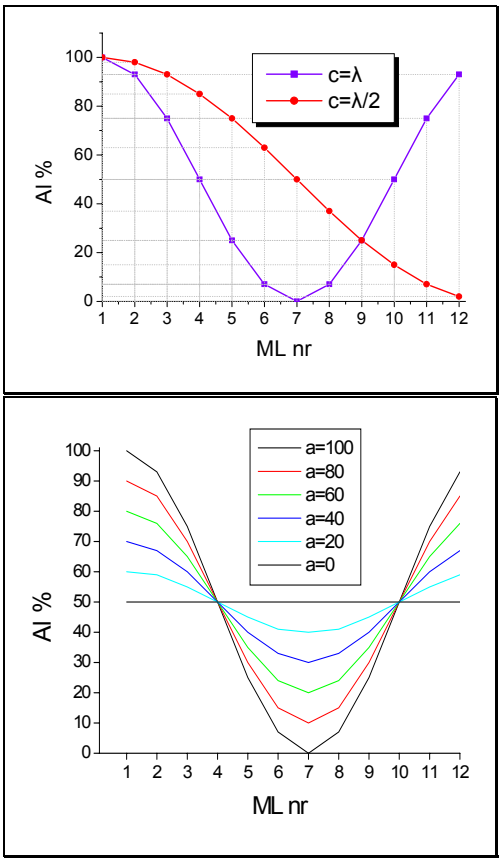

Fig. 2: Al percentage stoichiometry variation by monolayer

In order to produce the models we built a computer code where we can choose the periodicity along the [0001] direction, the size of the supercells along the (0001) planes, the type and amplitude of the modulation. The program in sequence produces the atomic positions of the wurtzite structure and populates the lattice with atoms. The Nitrogen layers are fully occupied by N atoms. For each of the rest of the layers, the program calculates the stoichiometry according to the modulation and randomly distributes the Al and Ga atoms in every plane. The stoichiometry of each layer can be put by hand or it can be calculated using a closed form, as we will show below.

There are many ways to modulate the stoichiometry. In the present study we investigate two types, each one to study a corresponding effect, i.e. one for the stoichiometry of the alloy and the other for the variation of the stoichiometry in the super cell. In the first type of modulation we choose a step like variation of the stoichiometry of Al, being 0 for μ layers and 1 for ν layers, $\nu + \mu = 12$, 7 or 2. This case is extreme and it is not expected to occur in the real alloys, but its study will give us an upper limit of the variations of the properties with this modulation. By changing ν we actually vary the stoichiometry of the sample. Therefore this type of modulation can help us access the upper limit of the effect of the LRAO on the properties as a function of sample stoichiometry.

For the second type of modulation, at constant stoichiometry, we have chosen harmonic modulations with wavelength some multiply of the periodicity along [0001] and different amplitudes. The sample stoichiometry is set to ½ and the variation of the stoichiometry from layer to layer is given by:

$$x=0.5+\alpha\cdot 0.5\cos(2\pi/\lambda)\cdot d\cdot \nu,$$

where, λ is the wavelength in units of the super cell periodicity, d is the interlayer spacing, α is the amplitude factor and ν is the index of layer for 7ML and 12ML periodicities. The variation of the stoichiometry for the two wavelengths and the amplitudes used in this study are shown in Fig. 2.

For both types of modulation we have produced the XRD patterns using the program ATOMS.

Results and discussion

In general the new periodicity of the crystal due to the modulation of the stoichiometry will introduce additional peaks of the type (000ξ) in the XRD patterns. If we follow the normal assignment of the peaks, then the (0002) peak of GaN should correspond to the (00024) peak of 12ML super lattice. This can make difficult the comparison between the structures. In order to facilitate the discussion and taking into account that for example for the 12ML there would be 12 new possible peaks, the 12th of them corresponds to the (0002), we will refer to the peaks as 1, 2, … n. Depending on the type of modulation and the amplitude some of the possible peaks may have very small amplitude or zero. The purpose of the following analysis is to find the signature of the stoichiometry modulation in the XRD pattern. In the following we will consider separately the cases of 2ML, 7ML and 12ML.

2ML periodicity.

In 2ML periodicity models, the normally forbidden (0001) peak (2θ=17.10°) is present (Fig. 3B). A linear dependence between (0001) peak's intensity and Al percentage in the 1st of the two monolayers revealed. (0001) peak's intensity is lower if Al also exists in the 2nd ML. In general, this peak is more intense in the cases where there is an alternation of Al and Ga monolayers.

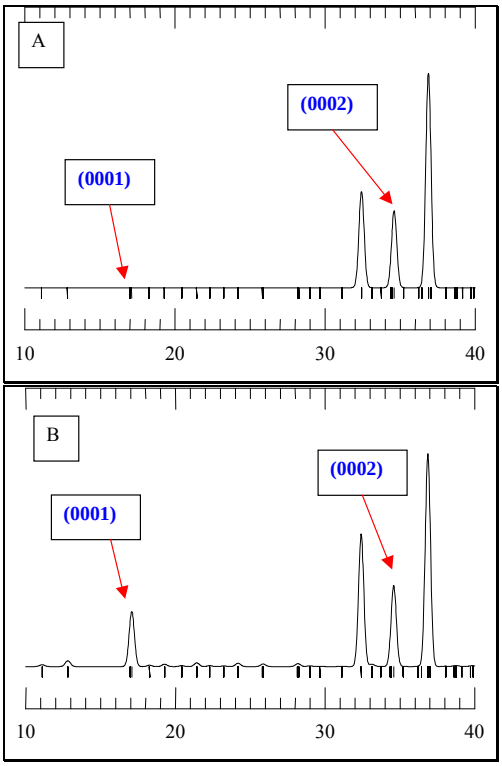

Fig. 3: 2ML XRD patterns A: 0%Al 0%Al B: 80%Al 0%Al

Type A modulation.

In Table 1 we show the intensities for the super lattice peaks for the type A modulation and for 12ML case. A rich behavior can be noticed by changing the number of Al layers present in the super cell. In some cases extinction of some peaks is observed. Also, we notice that the peaks have almost equal intensity for 1 and 11 Al layer/s and that the 1st, 2nd and (n-1) peaks increase as the number of Al layers increases, having a maximum at 6 layers, while the other peaks have values near the 500 counts. Similar results are obtained for the 7ML case. The peak corresponding to the (0001), is present only for odd Al layers.

Type B modulation.

Fig. 4 shows the results for two wavelengths and 12ML. One can observe that the 1st and (n-1) peaks are almost not effected, while the rest of the peaks for λ = 1/2 almost vanish. The effect of amplitude for a given λ and 7ML is shown in Fig. 5. We notice that the (0002) peak has the same intensity and that the intensities of the1st and (n-1) peaks vary linearly with the amplitude.

Discussion.

LRAO in AlGaN is a complicated phenomenon and many questions need to be answered. Experimentally (XRD) one observes many super lattice peaks, which indicate the presence in the sample of three new periodicities (2, 7 and 12) embedded in a random alloy phase. Therefore it cannot be expected theory to reproduce exactly the experimental results or propose a definite model.

	Peak order	1	2	3	4	5	6 (0001)	7	8	9	10	11	12 (0002)
	Cts/2θ (deg)	**2.8**	**5.7**	**8.5**	**11.4**	**14.2**	**17.1**	**20**	**22.9**	**25.8**	**28.7**	**31.6**	**34.6**
Al 100% ML	Ga ML												
0	12	0	0	0	0	0	0	0	0	0	0	0	7131
1	11	449	448	445	441	436	430	422	413	403	392	381	6769
2	10	868	775	629	441	226	0	218	413	570	679	736	6407
3	9	1227	895	445	0	319	430	309	0	403	785	1041	6046
4	8	1503	775	0	441	391	0	378	413	0	679	1274	5686
5	7	1676	448	445	441	117	430	113	413	403	392	1421	5328
6	6	1735	0	629	0	451	0	436	0	569	0	1471	4970
7	5	1676	448	445	441	117	430	113	413	403	392	1421	4615
8	4	1503	775	0	441	391	0	378	413	0	679	1274	4263
9	3	1227	895	445	0	319	430	309	0	403	785	1041	3913
10	2	867	775	629	441	225	0	218	412	569	679	735	3567
11	1	449	448	445	441	436	430	422	413	403	392	381	3226
12	0	0	0	0	0	0	0	0	0	0	0	0	2892

Table 1: cts – 2θ in 12ML periodicity

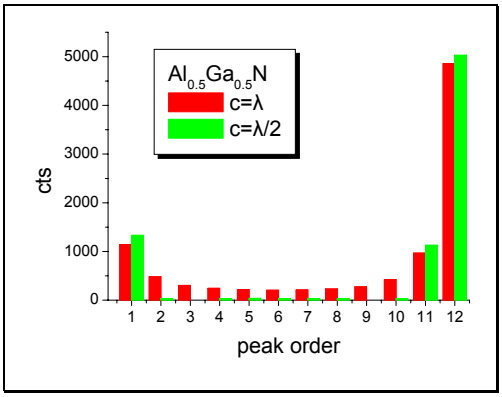

Fig. 4: Peaks variation due to stoichiometry modulation (counts – 2θ) in 12ML periodicity

In the light of the present results where we have well defined atomic arrangements we will discuss some experimental features. These features include the intensity of the peaks relative to the (0002) peak, their position, the absence of some of them, and the overall variation of the intensity of the peaks as we go from the 1st to the n – 1 peak. All the models we have examined have super lattice peaks which have the same relative intensity as the experimental peaks.

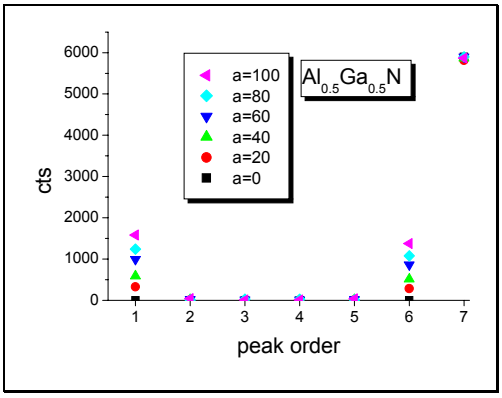

Fig. 5: Peaks variation due to stoichiometry modulation (counts - peak order) in 7ML periodicity

This is a confirmation that the effect observed experimentally has the expected magnitude. The fact that not all the possible peaks are observed experimentally can be understood to be due to the presence of some additional symmetry (Table 1), or to the experimental situation where the scattered X-rays pass through other regions of the sample and some of them become extinct. Coming to the overall variation of the peak intensities, we notice that experiment gives the highest intensity to occur for peaks near n/2, while theory consistently gives the 1st, 2nd, and (n-1) to be the highest in intensity, with the exception of some cases in Table 1. To reconcile this we may say that scattering produced by the LRAO component of the sample, which is embedded in the random alloy, arrives at the detector after being filtered by the random alloy. Therefore, it is the result of two scattering processes. On the other hand in the present models the XRD patterns are produced with the assumption of a single component. Much bigger and more complicated models are needed to study this case, and such study is in progress.

Conclusions

A set of super cells to model the phenomenon of LRAO in the AlGaN system is produced and the calculated XRD patterns are studied systematically. We have spanned both stoichiometry and modulations at given stoichiometry. A very rich behavior is found. The present results confirm that the experimentally observed super lattice peaks show the expected relative intensities for LRAO. Also the possibility of the extinction of some peaks is discussed. The overall change of the intensity of the super lattice peaks is found not to be consistent with experimental findings, a fact the can be attributed to complicated experimental situation compared to the well defined atomic structure in the models. Therefore there is a need to move to bigger models to include ordered as well as disordered regions.

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