

Quantitative Analysis of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ Thin Films by XPS

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$\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films prepared by molecular beam epitaxy showed unexpected electrical results and it was thought that the films might have compositions different from those intended. X-ray photoelectron spectroscopy (XPS) was used to determine the Al to Ga compositions of two films. The films had been exposed to air, so they had contaminant layers on them. This paper describes the approach taken to obtain an accurate measure of the Al to Ga compositions, and compares the results with those obtained based on a routine quantitative analysis, and by lightly sputtering the surface to remove contaminants.

1. Introduction

Most analysts use a very simple approach to obtain quantitative analysis of samples using x-ray photoelectron spectroscopy (XPS). The model assumes that the atomic concentration is uniform across the surface and with depth. When films that have been grown in ultra-high vacuum, for example by molecular beam epitaxy (MBE), are exposed to air, they will be contaminated and in general such a measurement would not be expected to provide a reliable result. Ideally, the compositions of MBE grown films should be determined by transferring them under vacuum to an analysis chamber but this is not always possible. Other approaches for quantitative analysis of contaminated films include making an allowance for the attenuation of the photoelectrons emitted from the underlying film by the contaminant overlayer, or by "lightly" sputtering the surface with inert gas ions to remove the contaminants. Such approaches are not necessarily easy or reliable. In the former approach, the electron attenuation lengths [1] in the contaminant layer need to be known. When sputtering is used to remove contaminants, preferential sputtering [2] could change the surface composition of the film.

The electrical properties of Si-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films grown on sapphire by molecular beam epitaxy (MBE) were being investigated as a function of Al mole fraction using temperature dependent Hall-effect measurements by colleagues in another laboratory, and the results were not as expected. The request was made to determine the Al to Ga compositions of two films with XPS. In this work, the different methods for quantitative analysis of the Al to Ga compositions of two MBE grown $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films were compared after having been exposed to air. For the as-received samples, the choice of peaks for quantitative analysis is discussed, and the effects of "light" sputtering on the quantitative analysis are also examined.

2. Experimental conditions

The $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers were grown with MBE using ammonia as the nitrogen source. Elemental Al, Ga and Si were supplied from standard Knudsen cells. A 20 nm AlN buffer layer was deposited at 800°C on $\text{Al}_2\text{O}_3(0001)$, followed by a 1.2 μm $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer [3]. Two samples were supplied, having x (Al) values of 0.5 and 0.3.

The XPS measurements were made using a Surface Science Instrument's (SSI) M-Probe. This instrument is equipped with a monochromatic Al x-ray source. An x-ray beam size of 400 mm x 1000 mm was used in this work. Survey scans from 0 – 1200 eV binding energy were made at an instrument resolution of 1.5 eV and 1 eV step intervals. Additional scans were also made from 60 – 180 eV at 0.2 eV step intervals. Acquisition times were 4 and 10 min, respectively.

Quantitative analysis was performed using the SSI software. The find-and-identify routine was used together with a linear background subtraction. Sensitivity factors were obtained from Scofield cross-sections that were adjusted by the sensitivity exponent that was measured from the instrument calibration menu.

Sputtering was done with argon ions at 3 keV, and the ion beam was rastered over a 4 mm x 4 mm area of the sample, ensuring a uniformly sputtered region for the analyzing beam of x-rays.

3. Results and discussion

3.1 Peak selection

Survey spectra from the two $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples are shown in Fig. 1. Besides the expected Al, Ga and N peaks, C and O contaminants are readily seen. Most software programs use the most intense photoelectron peak from each element in the quantitative analysis, and assume that the surface is uniform laterally within the analysis area, and uniform with depth. This is obviously not the case for these samples due

to the contaminant overlayers, so one would not expect to get accurate compositions using the standard quantitative analysis routine mentioned above. The most intense photoelectron peak from Ga is the $2p_{3/2}$ signal near 1117 eV binding energy, which corresponds to an electron kinetic energy of about 370 eV. The 2s and 2p intensities from Al are very similar to each other, and the corresponding electron kinetic energies are about 1369 and 1414 eV, respectively. These large differences in electron kinetic energies for Ga $2p_{3/2}$ and Al are the main reason why a quantitative analysis using the Ga $2p_{3/2}$ peak and either Al peak will be inaccurate. This is due to the fact that the lower kinetic energy Ga $2p_{3/2}$ photoelectrons will be attenuated more than the higher kinetic energy Al photoelectrons in passing through the contaminant overlayers. In C, electrons at kinetic energies of 370 and 1400 eV will have practical electron attenuation lengths of about 1.1 and 3.4 nm respectively [4].

Note that there are also weaker Ga photoelectron peaks at similar binding energies to the Al binding energies; for example, 160 eV (Ga 3s) and 105 eV (Ga 3p); see Fig. 1. Since these Ga and Al photoelectrons now all have very similar kinetic energies, they will be attenuated by very similar amounts in passing through the contaminant overlayers, and if these transitions were used, accurate quantitative analyses would be expected. Therefore, the four different

combinations of these Al and Ga peaks were used for quantitative analysis of the as-received samples, thereby giving a self-consistent check of the uncertainty in the results.

XPS scans from 60 – 180 eV binding energies from the two $Al_xGa_{1-x}N$ samples are shown in Fig. 2. Note that surface contamination from S is now also detected. The four different relative Al and Ga concentration measurements using the four different peak combinations of Al (2s or 2p) and Ga (3s or 3p) for each sample are listed in Table 1. For the $Al_{0.5}Ga_{0.5}N$ sample, all four measurements give very similar concentrations to each other, indicating a composition of $Al_{0.50}Ga_{0.50}N$ with an uncertainty of about 1 atomic percent. For the $Al_{0.3}Ga_{0.7}N$ sample, the actual composition is indicated to be $Al_{0.32}Ga_{0.68}N$, with a similar uncertainty. The fact that four different peak and sensitivity factor combinations produced such similar concentrations for each sample also supports the validity of this approach.

On reporting these results, it was found that some MBE samples had been mislabeled; hence the unexpected electrical results mentioned earlier.

The Al compositions of the $Al_xGa_{1-x}N$ films were then also determined by x-ray diffraction for samples with $x = 0.5$ and $x = 0.3$, and they were 51% and 31%, respectively [3]. These results are in very good agreement with the XPS calculations.

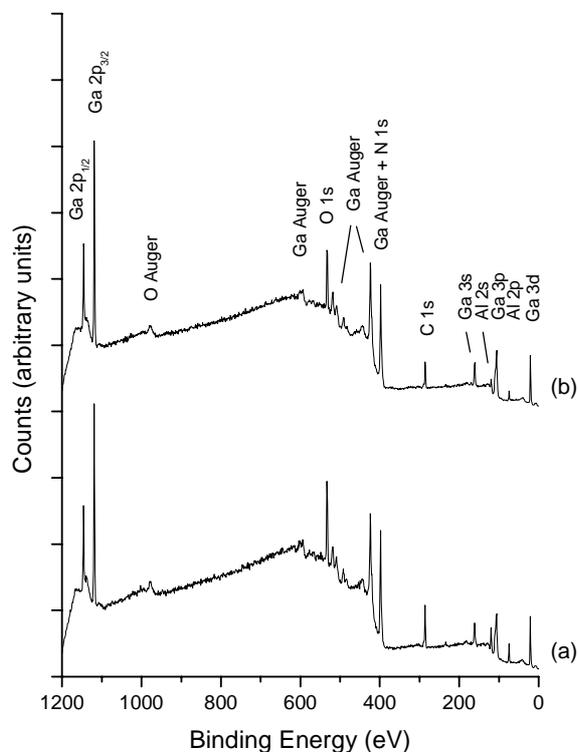


Fig. 1. XPS survey scans from the two $Al_xGa_{1-x}N$ samples, as received, (a) $Al_{0.5}Ga_{0.5}N$, and (b) $Al_{0.3}Ga_{0.7}N$. Note the C 1s and O 1s peaks from surface contamination. Each spectrum took 4 min to acquire.

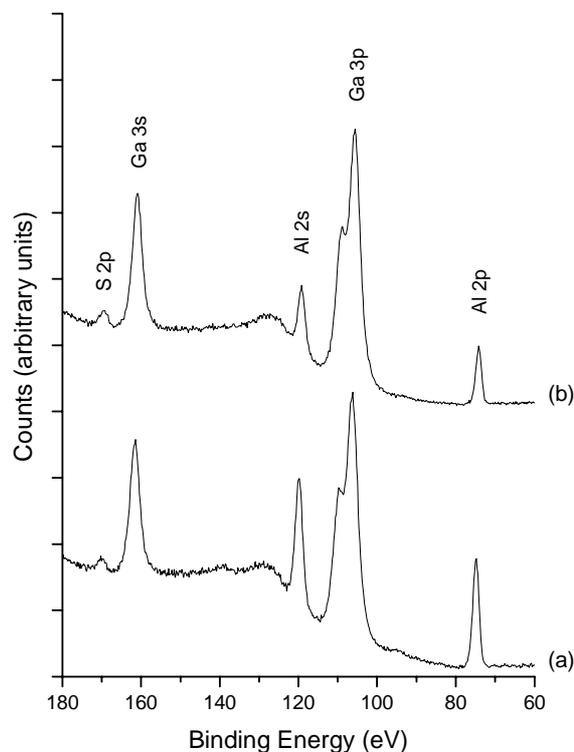


Fig. 2. XPS scans from 60 – 180 eV binding energies from the two $Al_xGa_{1-x}N$ samples, as received, (a) $Al_{0.5}Ga_{0.5}N$, and (b) $Al_{0.3}Ga_{0.7}N$. Note the small peak from S contamination on the surface. Each spectrum took 10 min to acquire.

Table 1 Al and Ga relative concentrations for each sample, measured using the four different combinations of Al and Ga photoelectron peaks that have similar electron kinetic energies.

Sample	Al (at %)	Ga (at %)	Photoelectrons Used
$Al_{0.5}Ga_{0.5}N$	50.9	49.1	Al 2p, Ga 3p
	50.3	49.7	Al 2p, Ga 3s
	49.6	50.4	Al 2s, Ga 3p
	49.0	51.0	Al 2s, Ga 3s
AVERAGES	49.9	50.1	
$Al_{0.3}Ga_{0.7}N$	33.0	67.0	Al 2p, Ga 3p
	33.1	66.9	Al 2p, Ga 3s
	30.9	69.1	Al 2s, Ga 3p
	31.0	69.0	Al 2s, Ga 3s
AVERAGES	32.0	68.0	

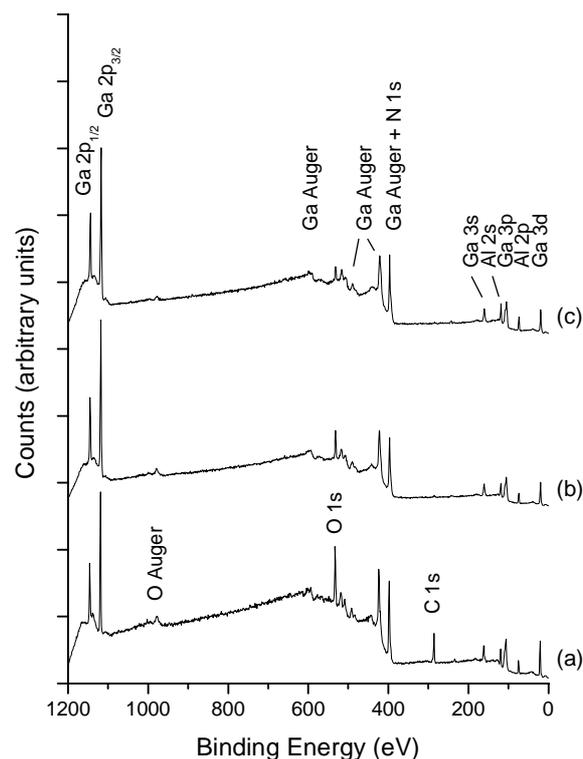


Fig. 3. XPS survey scans from the $Al_{0.5}Ga_{0.5}N$ sample, (a) as received, (b) after sputtering with Ar to remove the C, and (c) after sputtering to further reduce the O by 50%.

If the main Ga peak ($Ga\ 2p_{3/2}$) were used for quantitative analysis instead of the Ga 3s or Ga 3p peaks, the Ga concentration would be lower than the true value as the low kinetic energy Ga $2p_{3/2}$ photoelectrons would be attenuated much more than the Ga 3s or Ga 3p photoelectrons. For the $Al_{0.5}Ga_{0.5}N$ sample, using the $Ga\ 2p_{3/2}$ peak (and the homogeneous composition model) gives a composition of Al:Ga of 55:45 atomic percent, which is in error by 10%.

3.2 Effects of sputtering

As mentioned earlier, many analysts use “light” inert gas sputtering to remove surface contaminants in order to perform a quantitative analysis on the underlying film. In the case of $Al_xGa_{1-x}N$ films, preferential sputtering may occur and lead to an incorrect result, even with “light” sputtering. Errors produced in such an analysis with sputtering were also examined.

Sputtering was done in short intervals so that two scenarios could be examined. In the first case, sputtering was performed until no visible C peak was observed. In the second case, sputtering was continued until the oxygen intensity was further reduced by 50%. XPS survey scans of the

$Al_{0.5}Ga_{0.5}N$ sample before sputtering, after C removal, and after further oxygen removal are shown in Fig. 3. By examining the low binding energy peaks, it is readily observed that the Ga concentration decreases relative to the Al concentration with increased sputtering. After sputtering to remove the C, the measured Al:Ga ratio increased from 50:50 to 55:45 atomic percent, and after sputtering to reduce the O, the ratio increased further to 62:38 atomic percent.

The effect of using the $Ga\ 2p_{3/2}$ peak instead of the Ga 3s or 3p peaks, and the effects of Ar^+ sputtering on the measured Al and Ga relative concentrations, are listed in Table 2 for easy comparison.

4. Summary

It has been shown that for $Al_xGa_{1-x}N$ films, excellent quantitative analysis can be obtained for the Al:Ga relative concentrations without sputtering, when appropriate photoelectron peaks are used. The uncertainty is estimated as ± 1 atomic percent. It has also been shown that often-used “light” sputtering to remove contaminants cannot be used for $Al_xGa_{1-x}N$ films due to the preferential removal of Ga relative to Al.

Table 2. Al and Ga relative concentrations for $Al_{0.5}Ga_{0.5}N$ showing the effect of using Ga photoelectron peaks at very different kinetic energies, and the effects of sputtering with Ar^+ .

Peaks Used	Conditions	Al (at %)	Ga (at %)
High Kinetic Energy Al (2s, 2p), High Kinetic Energy Ga (3s, 3p)	As Received	50	50
High Kinetic Energy Al (2s, 2p), Low Kinetic Energy Ga ($2p_{3/2}$)	As Received	55	45
High Kinetic Energy Al (2s, 2p), High Kinetic Energy Ga (3s, 3p)	Sputtered to Remove C	55	45
High Kinetic Energy Al (2s, 2p), High Kinetic Energy Ga (3s, 3p)	Sputtered to Remove C	62	38

References

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