

## Applications Note

# XPS analysis of a N-doped GaAs thin film using Ag L $\alpha$ excitation

MO474(A)

**Keywords** Higher energy X-ray source, Ag L $\alpha$ , N-doped GaAs thin film.

### Overview

Nitrogen-doped GaAs (GaAs<sub>1-x</sub>N<sub>x</sub>) is finding application in high efficiency solar cells and vertical cavity surface emitting lasers (VCSELs). Nitrogen doping has been shown to cause perturbation of the host band structure. [1] Determination of chemical state and nitrogen concentration is pivotal in defining the material's electronic structure. X-ray photoelectron spectroscopy (XPS) is a commonly used technique for surface characterisation of this dilute N doped material.

In this application note we contrast the use of Al K $\alpha$  and Ag L $\alpha$  as excitation sources for XPS analysis of GaAs<sub>1-x</sub>N<sub>x</sub>. The advantage of using the higher photon energy excitation source to 'remove' overlapping Auger transitions with the N 1s core-level photoemission peak is demonstrated. Also introduced are advantages relating to the increased sampling depth provided by using the Ag L $\alpha$  excitation for characterisation of a thin-film material.

### Introduction

XPS is widely used for the analysis of complex materials, allowing the quantitative determination of surface chemical species. Surface analysis of transition metal compounds and alloys is an important application area for this technique. One of the most useful aspects of XPS analysis of these materials is the opportunity to quantify the surface species and investigate the oxidation states. However, the photoelectron spectrum can be complicated by the presence of Auger electron peaks, which occur due by the relaxation of the excited ion after ejection of the photoelectron.

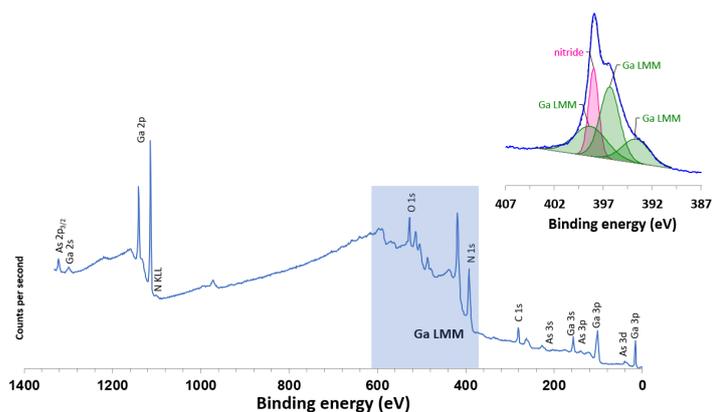
### Experimental

XPS results were acquired using the Kratos AXIS instrument with dual monochromatic Al and Ag excitation source. This accessory allows switching between Al and Ag X-ray lines automatically through the acquisition software. The process is fully automated using the instruments motorised X-ray monochromator and optional motorised dual anode (Al/Ag) X-ray source. The X-ray source is fitted with an anode that is 2/3 coated with Al and 1/3 coated with Ag. When changing from Al K $\alpha$  to Ag L $\alpha$  excitation motors move the anode relative to the filament such that X-rays are generated from the Ag portion of the anode.

The sample being characterised comprises a GaAs substrate which has undergone a nitridation process, forming an estimated 1 – 3 nm GaAs<sub>1-x</sub>N<sub>x</sub> thin film layer at the surface.

## Results and Discussion

The Al K $\alpha$  excited survey spectrum from a GaAs<sub>1-x</sub>N<sub>x</sub> thin film grown on a GaAs substrate sample is shown in figure 1. Photoemission peaks for constituent elements Ga, As and N are labelled, as well as those for surface contaminants carbon and oxygen. It is immediately apparent that there is a very strong contribution to the survey spectrum from the Ga LMM Auger transitions, bounded by the blue box. Significantly, these Auger transitions overlap with the N 1s and O 1s photoemission peaks. A high resolution, narrow region scan of the N 1s region is shown inset in figure 1.



**Figure 1: Al K $\alpha$  excited survey spectrum from GaAs<sub>1-x</sub>N<sub>x</sub> and (inset) N 1s/Ga LMM region high resolution scan.**

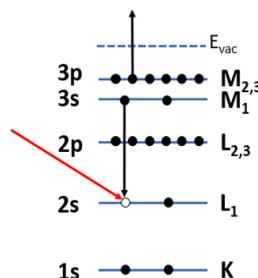
The N 1s/Ga LMM envelope results in a broad, complicated structure. A single symmetrical component is used for the N 1s peak with three broad peaks used to describe the Ga LMM transitions. Whilst the model is a good fit to the acquired data, with so many components it is conceivable that there is not a unique fit that correctly describes this envelope. This is problematic when the nitrogen concentration and chemical state is of fundamental importance for the performance of the material.

As briefly introduced above, the Ga LMM Auger peaks originate because of the relaxation of an excited Ga atom after ejection of the photoelectron. The core-hole, left behind by the ejection of the 2s (L<sub>1</sub>) photoelectron, is filled by an outer shell 3s (M<sub>1</sub>) electron. In this transition the electron moving to the lower energy level loses a quantum of energy equivalent to the energy difference of the two energy levels. This transition energy is coupled to a second outer shell electron 3d (M<sub>4,5</sub>). Where this energy is greater than the binding energy of the 3d electron, it is ejected from the atom as an Auger electron and is identified by the orbitals involved in the auto-ionisation process: LM<sub>1</sub>M<sub>4,5</sub>. This is shown in the schematic energy level diagram in figure 2. The energy of the Auger electron described in figure 2 is given by the equation:

$$E_{kin} = E_{L_{core\ state}} - E_{M_1} - E'_{M_{2,3}}$$

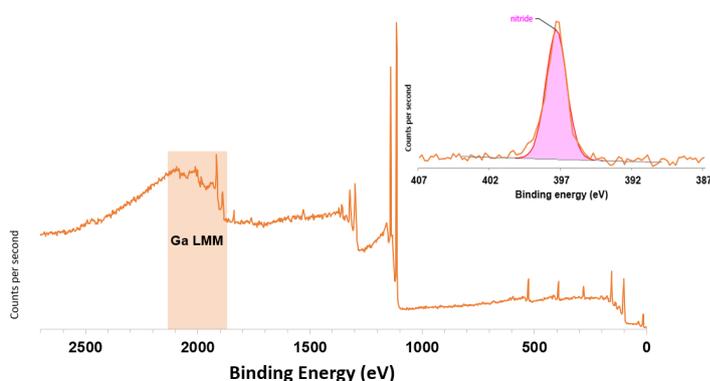
where  $E_{kin}$  is the kinetic energy of the ejected Auger electron,  $E_{L_{core\ state}}$  is the energy of the core shell and  $E_{M_1}$  and  $E'_{M_{2,3}}$  are the outer shell electron binding energies. Unlike the photoemission

process, it is evident that energy of the Auger electron is **independent** of the energy of the excitation source.



**Figure 2: Schematic diagram of process for creation of Ga LMM Auger electron.**

Figure 3 shows the survey spectrum from the same GaAs<sub>1-x</sub>N<sub>x</sub> sample excited using the monochromatic Ag L $\alpha$  excitation source.



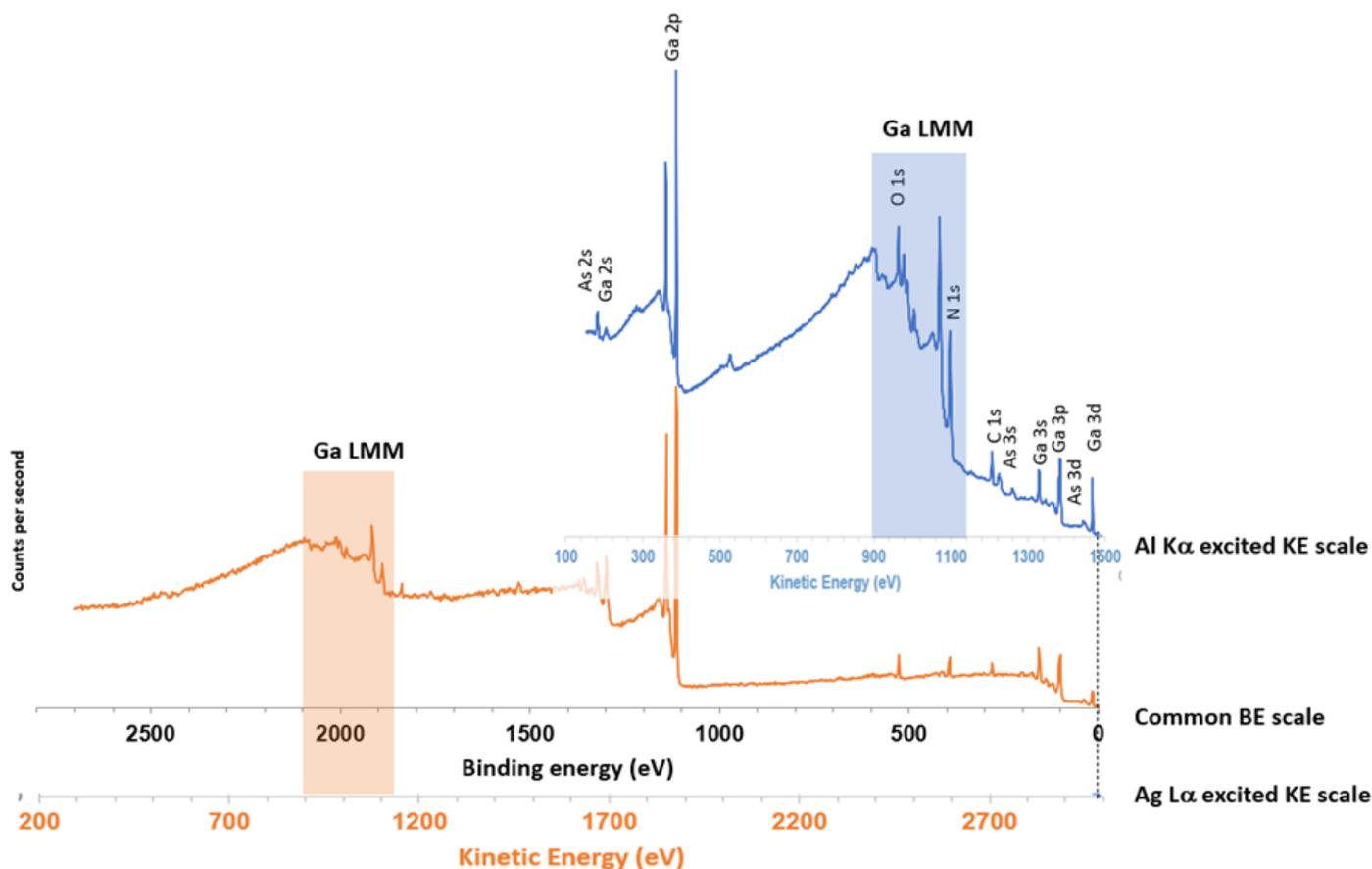
**Figure 3: Ag L $\alpha$  excited survey spectrum from GaAs<sub>1-x</sub>N<sub>x</sub> and (inset) N 1s region high resolution scan**

The photon energy of the Ag L $\alpha$  photons is 2984.2 eV which is 1497.6 eV higher energy than the Al K $\alpha$  used to excite the survey spectrum in figure 1. The effect of using the higher energy source is that all the photoelectrons have higher kinetic energy by virtue of equation 2

$$KE = h\nu - BE - \phi$$

where  $h\nu$  is the photon energy, BE is the (constant) binding energy of the electron core level,  $\phi$  is a constant spectrometer work function and KE is the kinetic energy of the ejected photoelectron. Although the measured KE of the photoelectrons has increased due to the increased photon energy, the KE of the Auger transition, which is independent of the photon energy remains constant. If the spectra are plotted as a function of binding energy, as shown in the overlay of Al K $\alpha$  and Ag L $\alpha$  excited survey spectra in figure 4, the core level photoemission peaks appear at the same binding energy. However, the Auger features appear shifted to 1497.6 eV higher binding energy.

Shifting of the Ga LMM Auger transitions by using the Ag L $\alpha$  excitation means that they no longer overlap with the N 1s photoemission peak, as shown in the inset high-resolution spectrum in figure 3. The Ag L $\alpha$  excited N 1s region gives a much simpler spectrum, with a single symmetrical peak centred at 397.6 eV. This corresponds to nitrogen in a nitride-like chemical environment. Removing the Auger transitions also



**Figure 4: Overlay of Al K $\alpha$  and Ag L $\alpha$  excited spectra with both binding and kinetic energy scales. The two survey spectra were normalised to the Ga 2p<sub>3/2</sub> peak height**

means that quantification of the survey spectrum easier. The relative elemental concentration of the elements is presented in table 1.

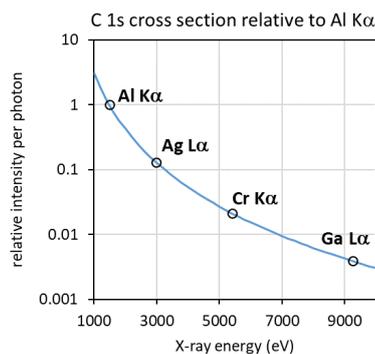
it is obvious that the peaks in the Ag L $\alpha$  excited spectrum are lower intensity than those excited by the conventional Al K $\alpha$  source.

Element	Core level	BE (eV)	RSF	Atomic conc. %	Error / %
C	1s	285.0	1.00	26.3	3.8
O	1s	531.6	2.93	17.7	1.7
N	1s	397.6	1.81	18.7	2.0
As	3d <sub>5/2</sub>	40.3	0.43	4.9	0.9
Ga	3d <sub>5/2</sub>	19.5	0.76	32.4	2.2

**Table 1: Relative atomic concentrations of thin-film GaAs<sub>1-x</sub>N<sub>x</sub> on GaAs substrate from Ag L $\alpha$  excited survey spectrum.**

Further comment is worthwhile on the relative intensities of the photoemission peaks and differences in sampling depths for core levels excited with the different X-ray sources with respect to characterisation of the GaAs<sub>1-x</sub>N<sub>x</sub> thin film.

It is known that the photoionisation cross sections for core level spectra decrease as the excitation energy increases [2,3]. This is shown in figure 5 by the plot of C 1s photoionisation cross section relative to Al K $\alpha$  excitation plotted as a function of excitation energy. It can also be observed qualitatively in the overlay survey spectra in figure 4. Comparing the relative intensities of the photoemission peaks at the low binding energy end of the spectra relative to the Ga 2p peaks in each spectrum



**Figure 5: Calculated C 1s photoionisation cross section plotted as a function of X-ray excitation energy, with commercially available HAXPES sources indicated.**

As highlighted by figure 5, the decrease in photoionisation cross section would be significantly worse for the more energetic hard X-ray sources, highlighting the benefit of the Ag L $\alpha$  source for this study.

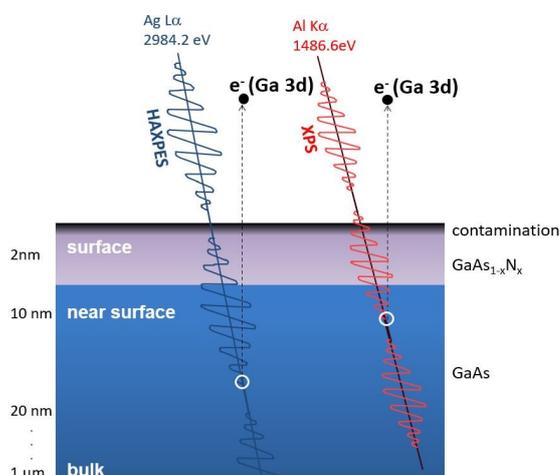
Comparing the high resolution N 1s regions excited with the two X-ray sources, it is evident that the decrease in photoionisation cross section for the Ag L $\alpha$  does not have too significant effect on the quality of the spectrum. Increasing the acquisition time from 60 seconds for the Al excited spectrum to 300 seconds for

the Ag excited spectrum results in spectra with similar statistics in terms of signal-to-noise ratio. The efficient collection and transmission of the generated photoelectrons by the spectrometer design mitigates the physical effect of generating fewer photoelectrons and ensures that high resolution spectra may be collected in sensible acquisition times, especially considering the relatively low dopant concentration of nitrogen in the thin film GaAs<sub>1-x</sub>N<sub>x</sub> for this sample.

transitions that overlap the N 1s photoemission peak when using conventional Al K $\alpha$  excitation are shifted to higher binding energy. This allows unambiguous curve fitting of a single N 1s component and identification of a nitride-like chemical state.

## References

- [1] A. Mascarenhas, Yong Zhang, "Electronic structure of nitrogen-doped GaAs and GaP," Proc. SPIE 10303, Gallium-Nitride-based Technologies: A Critical Review, 103030D (28 August 2002); <https://doi.org/10.1117/12.482617>
- [2] Curran Kalha et al 2021 J. Phys.: Condens. Matter in press DOI: 10.1088/1361-648X/abeacd
- [3] A. G. Shard et al., Surf. Interface Anal., 2019, 51, 763-773 DOI: 10.1002/sia.6647



**Figure 6: Schematic diagram of greater sampling depth for the same core-level excited with higher photon energy Ag L $\alpha$  X-rays.**

An advantage of using higher energy photon sources is the increased information depth that results due to the change in effective attenuation lengths of the electrons as they travel through the material. This is shown schematically in Figure 6. The greater kinetic energy of the same core level photoelectron when excited by the Ag X-rays relative to Al X-rays results in greater information depth. The fact that the Ga and As 2s photoelectrons will be more surface sensitive than the higher kinetic energy 3d photoelectrons allows qualitative and quantitative chemical state information to be derived as a function of depth without the need for angle-resolved XPS or destructive sputter depth profiling.

A final comment on quantification highlights that both the photoionisation cross section and the sampling depth are important considerations in generating quantitative results from this sample which is inhomogeneous as a function of depth from the surface. To generate a realistic quantification for the material, it is important that the photoemission peaks chosen for quantification have as similar kinetic energies, and therefore information depths, as possible.

## Conclusions

The Ag L $\alpha$  excitation source was used to acquire X-ray photoelectron spectra from a thin-film GaAs<sub>1-x</sub>N<sub>x</sub> grown on GaAs substrate. The use of the higher photon energy source has the significant advantage that the Ga LMM Auger

## Related documents online:

**MO405** Analysis of NiCoMn alloy with Ag L $\alpha$  X-rays

**MO461** Eliminating core line/Auger peak overlap using different photon energies