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COMMUNICATIONS

CONTRIBUTION TO THE QUANTITATIVE ANALYSIS OF TERNARY ALLOYS OF GROUP III–NITRIDES BY AUGER SPECTROSCOPY

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For correct quantitative interpretation of Auger spectra of group III-nitrides and their alloys it is necessary to have the relative sensitivity factors of elements and the sputtering yields measured for the material under analysis. These data are not available in the literature for those materials. In this work, the quantities have been determined experimentally that are needed for reliable and precise quantitative interpretation of Auger spectra of such materials, thus of AlN, GaN and their ternary alloys $Al_xGa_{1-x}N$. Measurements of reference AlN and GaN samples allowed to find the elemental sensitivity factors for these nitrides, and measurements on reference samples of ternary alloys $Al_xGa_{1-x}N$ allowed to find the ratio of the component sputtering yields, Y_{Ga}/Y_{Al}. It has been confirmed that if the relative sensitivity factors are obtained from measurements of reference samples of group III-nitrides, thus of compounds, and if in the alloys of such compounds no further change of the shapes of Auger peaks occurs, the both the areas below the Auger peaks in direct spectra and the Auger peak-to-peak heights in differentiated spectra can be used for quantitative analysis.

K e y w o r d s: GaN; AlN; $Al_xGa_{1-x}N$; AES relative elemental sensitivity factors; component sputtering yields Y_{Ga}/Y_{Al}

1 INTRODUCTION

Group III-nitrides have lately attracted significant attention for various electronic and optoelectronic applications. Many III-nitride-based devices involve heterostructures as the primary means for achieving improved performance. The properties of these alloys depend on the alloy composition. One of these alloys, AlGaN, is also used as a barrier material, its energy band gap depending on the AlN molar fraction. To determine the elemental composition and its depth distribution, Auger Electron Spectroscopy (AES) is one of the most widely used techniques. Even though depth profiling using this technique is nowadays already a standard procedure, there are still several areas in which a further development is needed. One of them is the accurate quantitative evaluation of the measured AES spectra, even in the case of nanometer layer structures based on chemical compounds, such as GaN, AlN, and of their alloys.

Whereas in the case of analysis of homogeneous alloys the accuracy of quantitative AES is relatively good, problems with accuracy are encountered when analyzing chemical compounds. In the former case one can use the Auger peak-to-peak heights (APPH) in differentiated spectra, $E * \mathrm{d}N(E)/\mathrm{d}E$, as a reasonable replacement for the Auger current, and the relative Auger sensitivity factors of pure elements determined from the heights of Auger peaks in $E * \mathrm{d}N(E)/\mathrm{d}E)$ spectra. These are modified so as to account for the quantities depending on the particular matrix (attenuation lengths of Auger electrons, back-scattering factor and sputtering yield) [1, 2]. In the case of chemical compounds the shapes of Auger peaks are usually changed in comparison with their shapes for pure elements and, as a rule, neither the Auger current nor the relative sensitivity factors determined from $\mathrm{d}N(E)/\mathrm{d}E$ spectra can be used. In these cases, both of these quantities have to be determined from the areas below the peaks. Determination of the area below the spectrum is a problem of its own: there are several methods how to define the curve of the background below the Auger peak [3–5].

Another factor that affects the accuracy of quantitative analysis is the change in the morphology, structure and chemical composition of the initial subsurface region due to the impinging ions used to depth-profile or to clean the sample. To cope with this negative phenomenon, one has to know the changes caused by ions for the particular material under analysis. The changes depend on the parameters of the ion beam (energy, kind of ions, angle of incidence) as well as on the material being analysed and stem from different component sputtering yields (preferential sputtering), atomic mixing and other phenomena caused by the interaction of the ion beam with the solid [6–11]. Though there are nowadays numerous simulation codes for describing and determining the sputtering yields by Monte Carlo method (TRIM, T-DYN, *etc*), reliable results can only be reached experimentally. Several procedures for experimental determination of the sputtering yields and preferential sputtering have been used [8, 12–15]. Nevertheless, the most reliable quantitative re-

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Table 1. AlN, GaN and $Al_xGa_{1-x}N$ samples with known composition used to find the relative elemental sensitivity factors and component sputtering yields in the ternary system $Al_xGa_{1-x}N$

sample	X in $Al_xGa_{1-x}N$	deposition	laboratory
70798	1	MBE	WSI, Mnchen
GS590	0.763	MBE	Cornell Univ, NY
GS425	0.47	MBE	Cornell Univ, NY
174	0.35	MOCVD	ZMN, Ilmenau
GS524	0.338	MBE	Cornell Univ, NY
163	0.16	MOCVD	ZMN, Ilmenau
59	0	MBE	ZMN, Ilmenau
59	0.13	MOCVD	JKU, Linz
61	0.16	MOCVD	JKU, Linz
96	0.19	MOCVD	JKU, Linz
322	0.23	MOCVD	ZMN, Ilmenau
39	0.27	MOCVD	JKU, Linz
29	0.31	MOCVD	JKU, Linz

Table 2. Experimental conditions of the measurements

Auger system	Primary electron energy (keV)	Primary electron incidence angle (°)	Angle of ion incidence (°)
AES with CHA	5	0	67.5
AES with CHA	25	0	67.5
AES with CHA	5	60	43.4
AES with CHA	25	60	43.4
AES with CMA	3	50	30

sults could by obtained using standard samples of comparable composition. If AES analysis involves also sputtering, and if the same experimental parameters are used in sputtering both the analysed and reference samples, then the experimentally determined elemental sensitivity factors account also for the relative sputtering yields of the elements.

For correct quantitative interpretation of spectra of chemical compounds and their alloys it is necessary to have the relative sensitivity factors of elements and the sputtering yields measured for the material under analysis [5]. These data are not available in the literature for the nitrides of group III elements and their alloys. The determination of concentration and depth distribution of Al in AlGaN alloys is highly important. The topic of this work has been experimental determination of the quantities needed for reliable and precise quantitative interpretation of the measured Auger spectra of materials based on gallium and aluminium nitrides and their ternary alloys. Relative elemental sensitivity factors and preferential sputtering yields have been measured of the components contained in these multicomponent materials.

2 EXPERIMENTAL

The fundamental condition for conducting this study is the existence of reference samples of known composition, thus of gallium and aluminium nitrides (GaN and AlN) and of their alloys with various contents of respective constituents Al and Ga ($Al_xGa_{1-x}N$). The used samples have been prepared in several laboratories by molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD), see Tab. 1. Their stoichiometry (composition of the AlGaN layers) was established by X-ray diffraction and spectroscopic ellipsometry.

AES measurements of the samples were performed in two AES systems, namely in an Auger Microlab 350 equipped with a concentric hemispherical analyzer (CHA), and a Varian Auger electron spectrometer equipped with a cylindrical mirror analyzer (CMA). In the case of using CHA, the energy spectra of the emitted electrons were measured in the direct $E * N(E)$ mode with a constant retard ratio, whereas in the case of the CMA they were detected in the differentiated mode $E * \mathrm{d}N(E)/\mathrm{d}E$. In both cases, sputtering was conducted by Ar ions using the EX 05 VG ion gun. Auger measurements employed the Auger peaks of Al (KLL), Ga (LMM) and N (KLL).

At present, many authors use the peak areas as well as peak-to-peak heights as a measure of Auger currents. The latter method is more usual in the case of alloys. In our study we used the Auger peak areas, after subtraction of the background and noise, as a measure of Auger intensities in integral spectra. This procedure was performed by the Shirley approximation [3]. For quantitative interpretation of differentiated spectra, the Auger peak-to-peak heights (APPH) were used. Such an approximation can be used in the analysis of GaN and AlN and of their alloys because no additional change in the shapes of the Auger peaks of the ternary alloy is observed in comparison with their shapes in GaN and AlN.

The quantification procedures for the binary semiconductors GaN, AlN and then for the $Al_xGa_{1-x}N$ material system were carried out for three various primary electron energies (3 keV, 5 keV, 25 keV). The experimental set-ups lead to the following experimental parameters, see Table 2.

3 RESULTS

3.1 Relative sensitivity factors for AlN and GaN

The relative sensitivity factors for aluminium, gallium and nitrogen were determined from measuring clean AlN, GaN and Cu samples under various experimental conditions (Tab. 1). The measurement of the sample had always been preceded by measuring a clean sample of Cu. The relative sensitivity factors were then determined with respect to the Cu (LMM) peak. The areas below Auger peaks in direct spectra and APPHs in differentiated spectra were processed in a standard way [16] taking into account the matrix correction factors, namely the back scattering factor, r, in the given nitride and in the reference sample (Cu), the atomic densities of the nitride and of the reference sample, and the attenuation lengths of Auger electrons, λ, in the considered nitride and in the reference sample. The values of the backscattering factor

Table 3. Relative elemental sensitivity factors of Al (KLL) and N (KLL) in AlN and Ga (LMM) and N (KLL) in GaN

Auger transition	Al (KLL) in AlN	N (KLL) in AlN	Ga (LMM) in GaN	N (KLL) in GaN
5 keV, 0°	0.160	0.220	0.212	0.140
25 keV, 0°	0.181	0.233	0.225	0.155
5 keV, 60°	0.227	0.203	0.258	0.111
25 keV, 60°	0.300	0.281	0.308	0.142
3 keV, 50°	0.360	0.412	0.496	0.214

Table 4. Component sputtering yields $Y_{\mathrm{Ga}}/Y_{\mathrm{Al}}$ for AlGaN

Experimental condition	$Y_{\mathrm{Ga}}/Y_{\mathrm{Al}}$ for AlGaN
67.5°, 1 keV, Ar	1.55
43.4°, 1 keV, Ar	1.5
50° 1 keV, Ar	1.5

were calculated using the relations of Shimizu [17], the attenuation lengths of Auger electrons were determined by the TPP-2M formulae [18] and after Jablonski [19]. The found relative sensitivity factors for Ga (LMM), Al (KLL) and N (KLL) in GaN and AlN for various experimental parameters are summarized in Tab. 3.

The results reveal a marked difference in the relative sensitivity factors for the peak of N (KLL) in AlN and in GaN. This is primarily a consequence of the different value of preferential sputtering of AlN and GaN.

3.2 Preferential sputtering of single elements in the $\mathbf{Al}_x\mathbf{Ga}_{1-x}\mathbf{N}$ system

For determining the component sputtering yields in the ternary system AlGaN, reference samples of ternary nitrides $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ with known composition were used as listed in Tab. 1. From the measured areas below the Auger peaks or from the APPHs in differentiated spectra, the surface concentration of single elements in AlGaN were calculated using the relative sensitivity factors of the particular ternary system shown in Tab. 3. Due to different sputtering yields, the composition of the surface layer of the multicomponent sample is changed during bombarding the sample by high energy ions in comparison with the bulk composition. Using the relation for a two-component system [20] we determined the component sputtering yields of Ga and Al from the measured surface concentration and the known bulk composition of the reference samples. The component sputtering yields characterize preferential sputtering of these elements in the ternary system AlGaN. Table 4 lists the ratios of the component sputtering yields, $Y_{\mathrm{Ga}}/Y_{\mathrm{Al}}$, for AlGaN for various experimental parameters.

4 CONCLUSIONS

By analysing the reference samples of AlN and GaN, the relative sensitivity factors have been determined for elements contained in these nitrides. By measuring the reference samples of ternary alloys of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ the component sputtering yield relations $Y_{\mathrm{Ga}}/Y_{\mathrm{Al}}$, have been determined. By applying the relative sensitivity factors and the component sputtering yields to ternary alloys of GaN and AlN, reliable and precise compositions of these samples have been found. It has been confirmed that if the relative sensitivity factors are obtained from measurements of reference samples of group III-nitrides, thus of compounds, and if in the alloys of such compounds no further change of the shapes of Auger peaks occurs, the both the areas below the Auger peaks in direct spectra and the APPHs in differentiated spectra can be used for quantitative analysis.

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