Bulgarian Chemical Communications, Volume 46, Special Issue A (pp. 246 – 250) 2014

Application of Isohypses method for AES quantification of semiconductor solid solutions

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Received April 17, 2014; Revised May 26, 2014

Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

The Isohypses method (IHM), previously used in energy dispersive X-ray microanalysis, is discussed as a tool for AES quantification of ternary and quaternary semiconductor quasi-binary solid solutions. It is with standards, which components are mainly with an unit less than those of the analyzed compound (The standards are peripheral points on the concentration triangle/square). For that reason a less number of standards are requested, which is a principal advantage of the IHM compared to the method of a complete standards' description. The method is based on the assumption, that when mixing binary systems in which the values of response of the A element are equal to each other, the response is not changed. As a procedure it consists of: I. Construction of a nomograph according to Auger standards data and, II. Determination by it the sample composition from the Auger intensities. The essence of the method is presented in the paper and the specifications required by the considered class compounds. Applications for $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$ and $In_xGa_{1-x}P_yAs_{1-y}$ are discussed.

Key words: Auger electron spectroscopy, AES analysis, Semiconductor solid solutions

INTRODUCTION

Three reasons make us to remind the already proposed Auger quantification by isohypses [1]: I. The semiconductor solid solutions continue to be of interest and a subject of scientific research; II. Miniaturization strengthens the AES analyses importance, but III. Still the accurate Auger quantification is problematic. The total calibration by standard compositions perhaps is most accurate, but the method' use is limited when the number of components is more than three.

The Isohypses method (IHM) for AES quantification is developed by analogy of its use in energy dispersive X-ray microanalysis [2]. The term "isohypse" (from Greek "hypsos" – height) is cartographic. There it means a line connecting the points with equal altitude, in our case, respectively, equal Auger signal.

The method is based on the assumption, that when mixing binary systems in which the values of response of the element A are equal to each other, the response is not changed. It can be shown that this leads to the conclusion that the composition' isohypses for ternary and quaternary solid solutions are straight lines.

It is not known someone to have used into Auger practice the IHM. Hoping to have followers we submit an IHM application for $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$ and $In_xGa_{1-x}P_yAs_{1-y}$ systems. This is new at this work and its essence. But preliminary the general IHM procedure is exposed briefly according to our work [1].

THEORY

First IHM quantification will be demonstrated for three-component system (A, B, C). The concentration triangle sides AB, BC and AC conform to the homonymous binary systems. Their Auger response characteristics (experimentally or theoretically obtained) are plotted on the ordinates K_A, K_B, K_C (Fig. 1). Through them, the binary compositions a', a", etc., are constructed by the signal intensities K_A^S, K_B^S, K_C^S of the analyzed specimen. They define the isohypses a'-a", b'-b", c'-c", which crossings form the searched composition triangle A'B'C'. Its sizes reflect the experiment precision and the applicability of the IHM. If they are small, it is possible to treat A'B'C' as a point. The atomic part of i^{th}-element, c_i^S, is equal to the distance from this point, O, to the ABC side, opposite to the i^{th}-apex, normalized to the altitude (e.g., c_B^S = OM/BS). Otherwise these operations are performed toward the centre of gravity of A'B'C'.

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Now it will be presented the possibility of applying the IHM to four-component solid solutions of the type $AB_{1-x-y}C_xD_y$ and $A_xB_{1-x}C_{1-y}D_y$. The concentration triangle is replaced by a tetrahedron. The composition of first type semiconductors (e.g., $GaAs_{1-x-y}P_xSb_y$) is represented by a triangle with apexes the binary compounds AB, AC, AD (GaAs, GaP, GaSb). The availability of the intrinsic standard (c_A = 50%) allows analysing similar to that from Fig. 1.

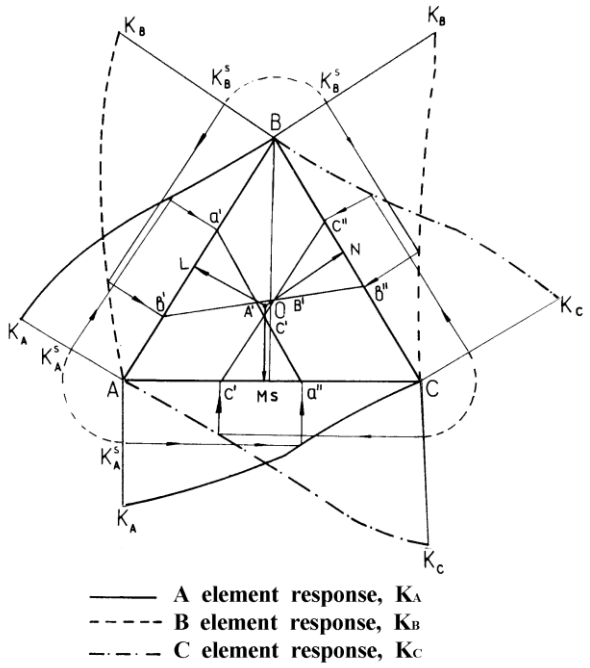

Fig. 1. IHM for a three-component system.

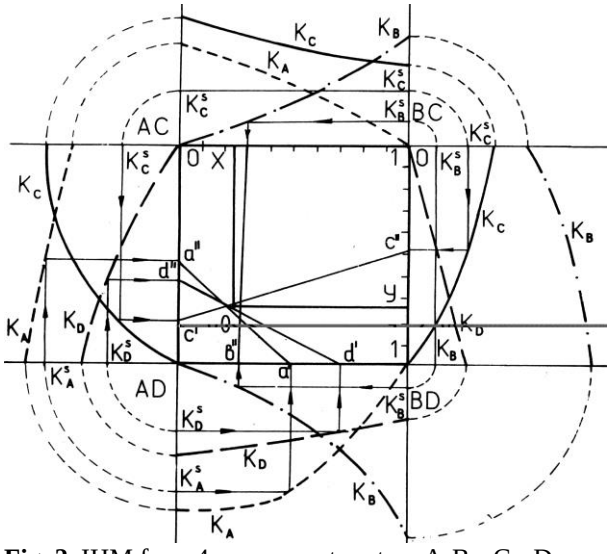

Fig. 2. IHM for a 4-component system $A_xB_{1-x}C_{1-y}D_y$.

The case of $A_xB_{1-x}C_{1-y}D_y$ appears to be more general and requires a detailed examination. All these compositions ($0 \le x \le 1$, $0 \le y \le 1$) correspond to the square tetrahedron' section with apexes AC, AD, BD, BC, shown on Fig. 2.

Again Auger response characteristics (now 3 each) are constructed on the figure' sides. The Auger signal of the i^{th}-element (for example, A) has intensity 0 along the side BC-BD. Starting at 0, it increases along BC-AC cut, it is biggest – but changes less – in AC-AD cut and decreases along BD-AD cut. The quantification is similar to that for the three-component system. The Auger signals obtained from the analyzed specimen K_i^S lead to the isohypses a'- a", etc. The figure of the errors is now a tetragon with its median point O. Since *x* varies (from 0 to 1) along the horizontal square' side and *y* – along the vertical, the distances of point O to the square side are just *x* and *y* content.

Nomograph Construction

IHM will be applied to the systems $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ at first. Their quasi-binarity is of main importance, giving the As contents c_{As} = 0.5. For $Al_xGa_{1-x}As$, it is located along the cut AlAs-GaAs (coincident with the As-isohypse) of the concentration triangle. The exclusion of As-side allows to present Fig. 1 simplified, as AlGaAs triangle tear in the top As and stood up straight: As-Al-Ga-As, Fig. 3 and Fig. 4. The points a' and a" (determining the isohypse for Al) and b' and b" (determining the isohypse for Ga) are found as in Fig. 1. The sought *x* is the medial between the points of intersection of these isohypses with the cut AlAs-GaAs. Now it becomes convenient to work with relative (toward As) Auger signals. The normalization is done by the value of the As-intensity from the stoichiometric binary composition (e.g., GaAs for the side As-Ga).

It seems a difficulty that on the mentioned sides there may not be the continuous solid solutions. But the ends and the middle point (i.e., As, GaAs, Ga) are enough to construct a "rough" response characteristic true reflecting analyses specificity. The fitting curve "Auger intensity vs. Ga contents" must be of "matrix correction" type:

$$y = x/[F + x(1 - F)] \qquad (1)$$

where F is the matrix correction factor (comprising the ion etching effects). The Ga (or As) contents in GaAs after etching must be known for curve' theoretic determination. The surface composition Ga/As (1keV Ar^+) is 1/0.92 [3] and the calculated "atomic density – attenuation length [4] – back-scattering factor" correction for Ga in GaAs is 0.94. So the dependence (1), (which is 0 at As and 1 at Ga), decreases with about 2% from the linear at 0.5, Fig. 3 and Fig. 4.

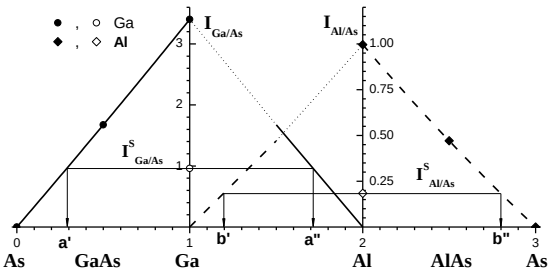

Fig. 3. IHM for the system $Al_xGa_{1-x}As$ (after Arthur's data [11]). The concentration triangle sides As-Ga, Ga-Al, Al-As are unfolded on the axis x, corresponding to 0-1, 1-2, 2-3.

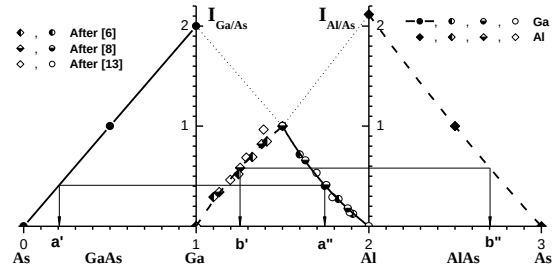

Fig. 4. IHM for the system $Al_xGa_{1-x}As$ (Bulk composition determined by the surface data).

But for the side Al-As we have neither AlAs standard, nor its sputtering data. Therefore getting the experimental intensity ratio Al/As^{GaAs} (The last symbol means that As is from GaAs) and correcting it by 1.14 (average from [5-8] for As^{AlAs}/As^{GaAs}), we obtain Al/As^{AlAs} 1.10. I.e. the relative (to As) Al-intensity is 0.55. This value for the compound AlAs is 0.51 (average from [9-12]), which gives for the mean of the side Al-As a decrease with about 7% compared to the linear dependency, Fig. 3 and Fig. 4.

As to the nomograph's part of the two elements from III group, it should not be forgotten that quasi-binary compounds are of analytical interest. So Auger behaviour of III-III alloys may not be useful to the response characteristics. It is more reliable the reconstruction to be made by the quasi-binars themselves. Assuming that these characteristics are proportional to the corresponding ones from the quasi-binary cut ($Al_xGa_{1-x}As$; $0 \le x \le 1$), so, the normalized Al characteristic at $x \le 0.5$ is Al/As from $Al_xGa_{1-x}As$ and that of Ga at $x \ge 0.5$ is Ga/As from $Al_xGa_{1-x}As$. (For the rest parts of the range these characteristics are not important: Ga and Al don't surpass 50% in the analyzed compositions.) If some of the metals (e.g., Ga) is characterized theoretically (in Part As-Ga of the *x* axis) and experimentally (in Part Ga-Al of the *x* axis), it is necessary to fit one curve to the other at the binary stoichiometric composition. This is most visible for In of Fig. 5.

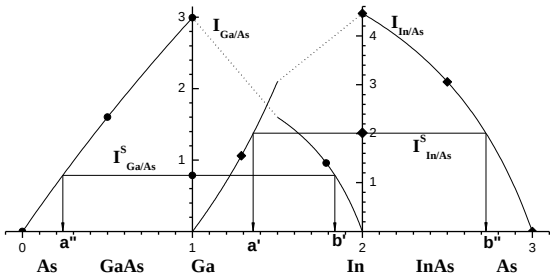

Fig. 5. IHM for the system $In_xGa_{1-x}As$.

The first $Al_xGa_{1-x}As$ application is after Arthur and LePore's work [11]. They analyse the surface composition, receiving linear dependency of *x* to Al/As (0.47 for AlAs) and Ga/As (1.67 for GaAs). As a standard we used their sample with (AlAs)-atomic part 0.42. Its relative intensities Al/As 0.18 and Ga/As 0.96 are constructed on Fig. 3, setting the points a' and a" for Ga' isohypse, and b' and b" for Al' isohypse. The concentrations are found from these points by a calculating procedure.

At the next application the bulk composition of $Al_xGa_{1-x}As$ layer is determined by the surface data. Influenced by the ion etching, now the Auger intensities are a non-linear function of *x*. They are found by a "matrix corrected" fitting of the data of several literary sets [6,10,13] (conformed with the analytical regime), Fig. 4. The medial composion from [10] is viewed as a sample, because it is located closest to the fitted curve.

By analogy the nomograph for the system $In_xGa_{1-x}As$ is constructed, Fig. 5. Now the construction of the response characteristics on the side Ga-In is by one experimental point. The ion etching is with 3 keV Ar^+. The composition of both standard and sample (3μm liquid-epitaxial layers on GaAs subsrate) is measured by the electron probe microanalysis. The very different sputtering behaviour of $In_xGa_{1-x}As$ and InAs makes worse the IHM analysis' result for this system.

$In_xGa_{1-x}P_yAs_{1-y}$ analysis is made by a specimen, which composition is measured by EPMA. Its Auger intensities (in arbitrary units) are Ga(30.5), In(133.0), As(52.5), P(22.0). We use the simplest model, accepting all response characteristics are straight lines connecting the binary apexes. The measured Auger intensities (in arbitrary units) are GaAs(132; 86), InAs(189; 58), InP(140; 116), GaP(104; 136); the figures in brackets correspond to the order of the elements in the formula. As this model allows to determine the isohypses' cuts by

simple trigonometric calculations, Fig. 6 displays only the isohypses.

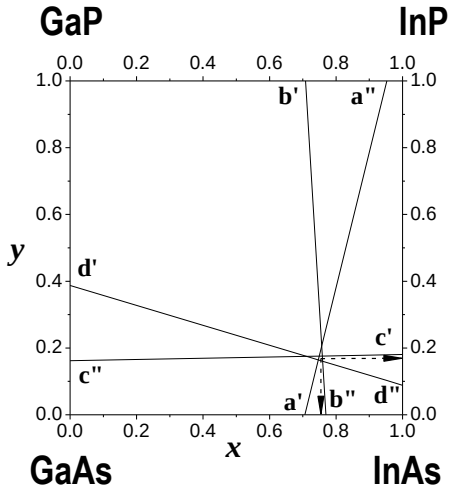

Fig. 6. IHM for the system $In_xGa_{1-x}P_{1-y}As_y$.

RESULTS AND DISCUSSION

The test of one method for quantification usually consists of evaluation by it of a standard (specimen with known composition), what we do. All received results are listed in Table 1.

Table 1. Quantification results

Specimen	True *x*	IHM *x*	Δ*x*/*x*, %	Δ*l*/*l*, %
$Al_xGa_{1-x}As$ [11]	0.42	0.41	2.4	1.2
$Al_xGa_{1-x}As$ [10]	0.51	0.56	10.1	1
$In_xGa_{1-x}As$	0.73	59	19.3	1
$In_xGa_{1-x}P_yAs_{1-y}$	0.74	0.75	2.4	0.7
(this row is to *y*)	0.17	0.17	1.6	0.8

The presented analytic applications prove that the isohypses method (IHM) is a useful and accurate tool for a quantitative Auger analysis (let remember that the elemental sensitivity factors method is semi-quantitative; the methods with one or two standards are very erroneous, while the method with fully tabulation is practically inapplicable for four-component compositions because of the great number of necessary standards). The standards' number for IHM is at least an order less (equidistant traveling over the figure periphery compared to that of its area).

Simpler compositions are used as the standards. Since their components number is usually less by one compared to the one of the analyzed, their preparation would offer no difficulty, too.

These standards are close to the analyzed specimen from physicochemical point of view (lattice type and constant, orientation, density, etc.). On the other hand, this closeness is the general condition for the matrix effects decrease, which increases the linearity of the analysis.

The IHM combines the taking into account of all matrix effects (inherent of the method used a series of compositions as standards) with applicability to quaternary compounds.

The IHM procedure is easy and leads to unambiguous result.

The work demonstrates that the Auger response characteristics can be received not only experimentally, but also by modelling. That's why a partial lack of experimental data is not an obstacle to the method utilization.

CONCLUSION

The Isohypses method is concretized and tested for AES quantification of a few ternary and quaternary quasi-binary solid solutions. It proves to be adaptable and accurate enough.

The Isohypses method' advantage is the using of less in number and simpler in composition standards, close to the analyzed sample.

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ПРИЛОЖЕНИЕ НА МЕТОДА НА ИЗОХИПСИТЕ ЗА ЕЛЕКТРОНЕН ОЖЕ СПЕКТРОСКОПСКИ КОЛИЧЕСТВЕН АНАЛИЗ НА ПОЛУПРОВОДНИКОВИ ТВЪРДИ РАЗТВОРИ

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Постъпила на 17 април 2014 г.; Коригирана на 26 май 2014 г.

(Резюме)

Разисква се количествен Оже електронен спектроскопски анализ на тройни и четворни полупроводникови квазибинарни твърди разтвори посредстом Метода на изохипсите, МИХ (вече използван в рьонгеновия микроанализ). Методът е със стандарти, като броят на елементите, които те съдържат, е поне с единица по-малък от този на анализирания състав – стандартите се явяват точки от периферията на концентрационния триъгълник/квадрат. Оттук, по-малкият брой необходими стандарти – основно предимство на МИХ спрямо метода на пълно привързване към стандарти. В основата на МИХ е приемането, че при смесване на бинарни системи с равни сигнали от елемента А, сигналът не се променя. Процедурно методът се състои от: I. Построяване на номограма по данните на стандартите; и II. Определяне чрез нея на състава на образеца по Оже интензитетите му. В статията е представена същността на метода и спецификата, налагана за разглеждания клас съединения. Разисквани са 4 приложения за $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$ и $In_xGa_{1-x}P_yAs_{1-y}$.