Journal of ELECTRICAL ENGINEERING, VOL. 52, NO. 5-6, 2001, 162–165

COMMUNICATIONS

QUANTITATIVE AUGER DEPTH PROFILING OF Ni/C MULTILAYERS BY FACTOR ANALYSIS AND COMPARISON WITH T–DYN SIMULATIONS

Jozef Liday * – **Miroslava Čatárová** * – **Eva Matušková**
Rastislav Kosiba * – **Gernot Ecke** ** – **Peter Vogrinčič** * – **Juraj Breza** *

The paper presents the measured depth distribution of elements and of their chemical states in a Ni/C multilayered structure prepared by pulse laser deposition (PLD), the thicknesses of respective layers being $d_{\mathrm{C}} = 1.7$ nm and $d_{\mathrm{Ni}} = 2.1$ nm. By simulating the sputtering process and applying factor analysis to the measured Auger depth profiles we have found that the measured depth distribution is notably affected by the process of sputtering (mainly by atomic mixing and preferential sputtering), and that nickel and most likely also carbon are contained in the multistructure in two basic chemical states, namely as pure elements and as a carbide.

K e y w o r d s: Auger electron spectroscopy (AES), quantitative AES, depth profiling, factor analysis, simulation of sputtering

1 INTRODUCTION

Recently, materials modified on a nanometer scale have became a topic of particular interest. Their properties are primarily preconditioned by the dominant influence of interface regions [1]. Such materials include also Ni/C multistructures comprising alternating nickel and carbon layers. Owing to appropriately different electron densities of the two materials, these multistructures exhibit high reflectivity for soft X-rays, which is why they are suitable for X- ray optical elements, for instance for mirrors and monochromators [2].

In thin Ni/C layers, the presence of two phases was observed [3]. In layers grown at temperatures close to room temperature at a low *rf* power, the structure consisted of crystalline *fcc* nickel and an amorphous carbon component. Films grown at higher temperatures and bombarded by energy particles are characterized by Ni_3C crystallites dispersed in an amorphous Ni-C mixture. Ni/C structures have a weak trend to form Ni_3C. Analysis of Ni/C multistructures of nanometer sizes prepared by pulse laser deposition (PLD) has shown that single layers generally do not contain just one component. In particular the Ni layer has a high content of carbon (up to 14 at%) [4].

One of the most widely used techniques for elemental analysis of surfaces and, in combination with ion sputtering, also for depth profiling is Auger electron spectroscopy (AES). Whilst in the case of analysis of uniform alloys, thus when the positions and shapes of Auger peaks are not affected by chemical bonds between elements, methods utilizing the sensitivity factors of pure elements [5] are used for quantitative interpretation of the measured Auger signals, in analyses of chemical compounds, in which the positions and/or shapes of Auger peaks often change, the use of such a procedure is strongly limited. These procedures can only be applied to chemical compounds, such as oxides, nitrides and carbides, for which it is possible to prepare well-defined reference samples and experimentally to determine the elemental sensitivity factors. Problems are encountered mainly in the analysis of elemental depth profiles, when the same element is present in several chemical states or if the chemical bonds vary with the depth. Under such situations it is advisable to use the Auger spectrum in the whole range of a given Auger peak for quantitative interpretation [6]. For this purpose, the method of factor analysis finds application ever more often. The factor analysis yields three highly important results: first, the number of fundamental chemical states (components) comprised in the sample, second, the spectra of single components, and, finally, their concentrations.

The fundamental equation for applying the factor analysis for quantitative interpretation of the measured data of a depth profile consisting of n consecutive energy spectra (steps of sputtering), each spectrum having m points, takes the form

$$\mathbf{D}_{m,n} = \mathbf{R}_{m,n} \cdot \mathbf{C}_{n,n} \tag{1}$$

where $\mathbf{D}$ is a data matrix, $\mathbf{R}$ is the matrix of abstract components, and $\mathbf{C}$ is the matrix of abstract concentrations. Decomposition of data matrix $\mathbf{D}$ into a product of

* Department of Microelectronics, Faculty of Electrical Engineering and Information Technology Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia
** Institut für Festkörperelektronik, Technische Univesität Ilmenau, Postfach 100565, Ilmenau, Germany

ISSN 1335-3632 © 2001 FEI STU

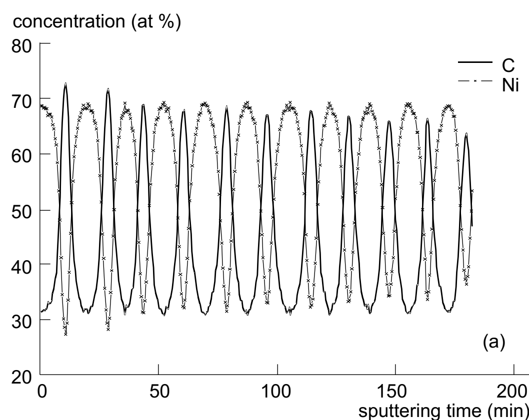

Fig. 1a Concentration depth profiles of the first eleven pairs of layers in the Ni/C multistructure obtained by sputtering by Ar^+ ions.

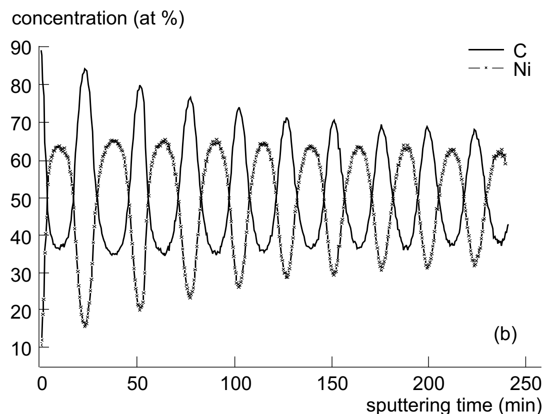

Fig. 1b Concentration depth profiles of the first eleven pairs of layers in the Ni/C multistructure obtained by sputtering by Xe^+ ions.

matrices **C** and **R**, and the further procedure of quantitative analysis are described in detail in [7].

This work is concerned with determining the depth distribution of elements and of their chemical states in a Ni/C multilayerd structure by AES.

2 EXPERIMENT

Ni/C multilayered structures were manufactured by PLD at the Frauenhofer Institute for Materials and Beam Technology in Dresden. On a (100)-oriented Si substrate, 75 pairs of carbon and nickel layers were deposited, with a carbon covering layer on top. The thicknesses of respective layers were $d_{\mathrm{C}} = 1.7$ nm and $d_{\mathrm{Ni}} = 2.1$ nm, as found by X-ray reflectometry.

To determine the relative sensitivity factors of C in graphite form (KLL peak at 272 eV), of Ni (58 eV MNN and 848 eV LMM), and to obtain reference spectra for factor analysis, reference samples were used that were prepared by magnetron sputtering of C and Ni on Si substrates. The relative sensitivity factor for carbon chemically bound with nickel in the form of a carbide as well as its reference spectrum were obtained directly from AES measurements of the concentration depth profile in the region of the nickel layer.

Auger analysis was carried out in an Auger spectrometer Varian equipped with a cylindrical mirror analyzer (CMA) with variable energy resolution. A primary electron beam was used with an energy of 3 keV, diameter of about 10 μm and angle of incidence 15° with respect to the surface normal. Sputtering was achieved by scanned Ar^+ and Xe^+ ion beams with energy 1 keV and angle of incidence 65° with respect to the surface normal. The current of the ion beam was 11 nA for both of the noble gases used. The set slit of the CMA ensured an energy resolution $\Delta E/E = 0.6\%$, and sputtering was performed continually.

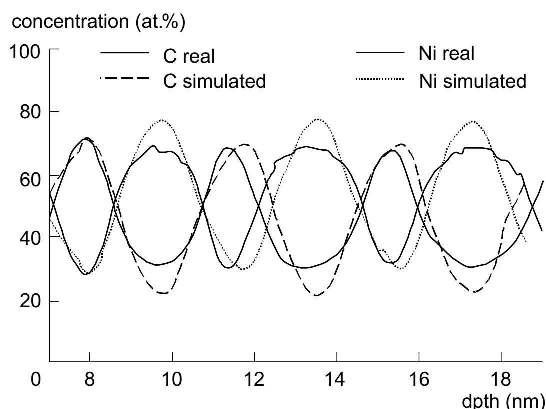

Fig. 2. Part of the measured and simulated depth profile of the Ni/C multistructure sputtered by 1 keV Xe^+ ions.

3 RESULTS AND DISCUSSION

The depth profiles of the topmost eleven pairs of layers in the Ni/C multistructure obtained by sputtering with Ar^+ and Xe^+ ions are in Figs. 1a and 1b. The spectra were evaluated by the common quantitative procedure making use of the elemental sensitivity factors [5]. One can see that in all nickel layers also some carbon was detected, and vice versa, in all carbon layers there was some content of nickel. As it was proved by simulating the depth profiles of these Ni/C multistructures under identical conditions, this fact is, to a remarkable degree, a consequence of the sputtering process itself, mainly of atomic mixing and preferential sputtering. The simulations were performed using the computer code T-DYN [8] completed with a program allowing for the influence of the electron escape depth [9]. Comparison of the measured and simulated depth profiles, shown in Fig. 2, reveals also that the measured contents of carbon in nickel layers were markedly higher than those obtained by sim-

ulation. This fact indicates that part of the carbon detected in nickel layers might have been incorporated in these layers already during the preparation of the multistructure.

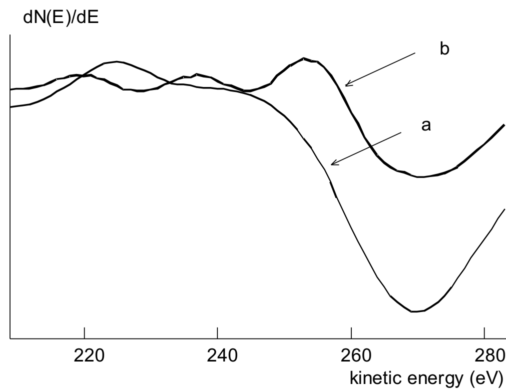

Fig. 3. Typical Auger peaks of carbon measured (a) in carbon and (b) in nickel layers of the Ni/C multistructure.

Figure 3 shows typical Auger peaks of carbon measured in carbon (a) and nickel (b) layers of the Ni/C multistructure. Whilst the shape of the peak of carbon detected in C layers corresponds to the graphite phase, the peak shape in Ni layers is typical for carbide. To assess the abundance of the two phases of carbon in respective layers of the Ni/C multistructure, analysis of the measured data of the depth profile was carried out by means of factor analysis making use of the computer codes described in detail in [10, 11]. Because of an excessive size of the data file of the measured depth profiles and thereof resulting requirements on the computer memory, factor analysis was performed for only the data matrix of carbon and in only three selected pairs of layers in the multistructure. Even though we found already in the first step of factor analysis that three forms of carbon were present in the data matrix, thus carbon in three chemical states, reference spectra of carbon contained in only two phases - graphite and carbide - were used for further analysis. The spectrum of graphite was obtained by analyzing a carbon layer prepared by magnetron sputtering on a silicon substrate. Since no reference sample of nickel carbide was available, the spectrum of carbon contained in carbide was obtained directly from AES measurements of the depth profile in the region of a nickel layer. Such an approach was substantiated by the following facts: The measured Ni/C multistructure did not contain any other elements except of Ni, C and Ar and Xe. The two latter ones come from the gases used for sputtering. The application of factor analysis to the data matrix of nickel revealed the presence of only two different states of nickel in the multistructure, see Fig. 4, most likely of pure Ni and nickel chemically bond with carbon in the form of carbide, thus only one species representing a chemical bond of nickel with carbon. Since carbon and nickel are present in the multistructure just in one chemical compound or phase, and because of the absence of other elements in the structure the chemical bond of C with another element is ruled out, the retrieved third shape of spectrum is most likely just a shift of the measured peak, to which the program for factor analysis is very sensitive. The detected weights of the two phases of carbon in the Ni/C multistructure sputtered by an Ar^+ ion beam are shown in Fig. 5. In this figure, the third plotted line represents a constant which was inserted into the program for factor analysis instead of the third observed phase.

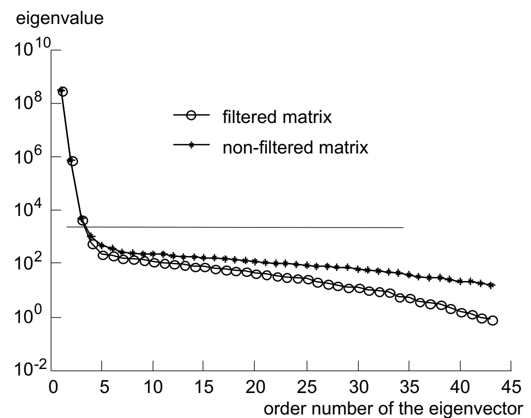

Fig. 4. Determination of the number of components in Ni matrix (two components).

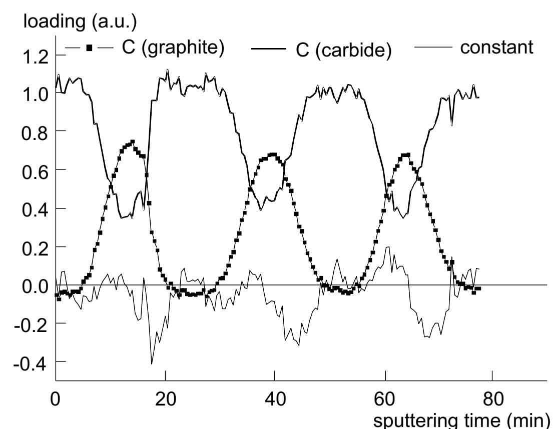

Fig. 5. +The weights of single phases of carbon in the Ni/C multistructure sputtered by a 1 keV Ar^+ ion beam.

4 CONCLUSIONS

The comparison of the measured and simulated depth profiles of the Ni/C multistructure prepared by PLD proves that Auger electron spectroscopy combined with ion sputtering provides reliable data on the depth distribution of elements in multilayered structures in which the thicknesses of single layers are very small, down to about

1.7 nm. The measured distribution of elements is notably affected only by the phenomena of sputtering (mainly by atomic mixing and preferential sputtering), which points at sharp, abrupt interfaces between the layers of Ni and C. This fact predestinates such Ni/C multistructures as calibrated samples for measurements and comparisons of the depth resolving power of surface sensitive techniques used for depth profiling.

The application of factor analysis to the measured Auger spectra profiles of elements in the Ni/C multistructure revealed that nickel and most likely also carbon were present in two basic chemical states, namely as pure elements and in the form of carbide.

Acknowledgement

The work was supported by grant No 1/5100/98 VEGA of the Ministry of Education of the Slovak Republic.

References

[1] KRAWIETZ, R. *et al*: Fresenius Journal of Analytical Chemistry 353 (1995), 246-250.

[2] McWHAN, D. B.: Synthetic Modulated Structures, Edited by Chang, L. L., Academic Press, New York,(1985), pp. 43-74.

[3] LAIDANI, N. *et al*: Surface and Coatings Technology 100-101 (1998),, 116-124.

[4] KHARLAMOV, V. *et al*: Physica Status Solidi (a) 166, 91 (1998) 95..

[5] LIDAY, J.—HOFMANN, S.—HARMAN, R.: Vacuum 43 (1992), 331-339.

[6] STRAUSSER—Y. E.—FRANKLIN, D.—COURTNEY, P.: Thin Solid Films 84 (1981), 145.

[7] MALINOVSKI, E. R.: Factor Analysis in Chemistry, 2nd ed., John Wiley & Sons, New York, 1991.

[8] BIERSACK, J. P.—BERG, S.—NENDER, C.: Nuclear Instruments and Methods B59/60 (1991) 21.

[9] KUPRIS, G.: Computersimulation von Atomic-Mixing in der Augerelektronen- spektroskopie, Verlag Shaker, Aachen, 1995.

[10] ČEŠKO, I.: Factor analysis in Auger Electron Spectroscopy (Faktorová analýza v Augerovej elektrónovej spektroskopii) Diploma work, FEI STU Bratislava, 1998. (in Slovak)

[11] PIETERWAS, R.: Quantitative Auswertung von Schichtsystemen auf Silizium mit der Faktoranalyse in der Auger - Elektronen - Spektroskopie, Dissertation zur Erlangung des akademischen Grades Doktor - Ingenieur, TU Ilmenau, 2000.

Received 20 January 2001

Jozef Liday (Doc, Ing, CSc) graduated in solid state physics in 1968 and received his PhD in electronics and vacuum technology, both from the Slovak University of Technology, in 1985. His teaching and research activities include materials analysis, thin films and surface science.

Miroslava Čatárová (Ing) was born in Trenčín in 1977. She graduated in microelectronics from the Slovak University of Technology, in 2001. Currently is a PhD student at the Department of Microelectronics. Her activities are directed particularly to materials analysis by quantitative Auger electron spectroscopy.

Eva Matušková (Ing) was born in Žiar nad Hronom in 1977. She graduated in microelectronics from the Slovak University of Technology, in 2001, and in marketing from the University of Economy in Bratislava in 2000. Currently is with Arthur Andersen Company, Bratislava.

Rastislav Kosiba (Ing) was born in Bratislava in 1974 and graduated in microelectronics from the Slovak University of Technology, in 1998. He has been a PhD student, since 1998 staying at the Technical University of Ilmenau, Germany.

Gernot Ecke (Dr, Ing) was born in Calbe, Germany in 1958. He graduated in electronic devices from TU Ilmenau in 1983, and gained the PhD degree in 1986. Since that time he has been Assistant Professor. His teaching and research activities include surface science and materials analysis. Biography not supplied

Peter Vogrinčič (Ing), born in Bratislava, in 1952, graduated in radio-electronics from the Slovak University of Technology, in 1992. Currently he is engaged in research at the Department of Microelectronics. His activities are directed particularly to quantitative Auger analysis and depth profiling.

Juraj Breza (Doc, Ing, CSc), born in Bratislava in 1951, graduated in solid state physics in 1974 and received his PhD in electronics and vacuum technology, both from the Slovak University of Technology, in 1982. Since 1985 he has been Associate Professor for microelectronics. His teaching and research activities include materials analysis, thin films and surface science.