Journal of ELECTRICAL ENGINEERING, VOL. 54, NO. 1-2, 2003, 52–56

COMMUNICATIONS

AUGER DEPTH PROFILING AND FACTOR ANALYSIS OF SPUTTER INDUCED ALTERED LAYERS IN SiC

Rastislav Kosiba [*] [**] — **Gernot Ecke** [*] — **Jozef Liday** [**]
Juraj Breza [**] — **Oliver Ambacher** [*]

The thickness of the altered layer created by ion bombardment of the 6H silicon carbide single crystal was determined by means of Auger depth profiling combined with factor analysis. After pre-bombardment of the surface until the steady state by argon ions with energies 1, 2 and 4 keV, the micro profiles of the altered layers were recorded by sputtering with low energy argon ions of 300 eV. As the position and shape of the carbon Auger signal depend on the perfection of the crystalline structure, they were used for depth profile evaluation by factor analysis. In this way the depth profiles of the damaged surface region could be estimated in dependence on the ion energy. The thickness of the altered layer of SiC bombarded with keV Ar ions using an incident angle of 80° was obtained.

K e y w o r d s: sputtering, altered layer, AES, depth profiling, implantation, silicon carbide, factor analysis

1 INTRODUCTION

Various steps in device technology as well as a number of surface sensitive analytical techniques often employ sputtering of the surfaces under study by ions. A surface sensitive analytical technique like Auger electron spectroscopy (AES) in combination with low energy ion sputtering is a valuable tool for high resolution depth profiling. However, sputtering of the surface by energy ions often brings about changes in morphology, structure an composition of the subsurface region, giving rise to an altered layer with characteristics different from those of the bulk. The thickness of the altered layer and its properties depend on the ion beam parameters (energy, ion species, angle of incidence) as well as on the investigated material itself. AES is a well suited method for investigations of the sputter induced compositional micro profiles close to the surface [1] and for thickness determination of the altered layer. One of the methods how to investigate the properties of such altered layers is sputter depth profiling of the altered layer under conditions of very shallow ion damage, *ie*, with a grazing incidence angle and/or with a use of low energy ions (some hundreds of eV) [2].

The present paper reports on investigations of the altered layers of SiC single crystal surfaces due to ion bombardment. Compositional changes at the silicon carbide surface caused by low energy ion bombardment are not well understood up to date. Publications with very different results can be found in the literature reporting on preferential sputtering and accompanying surface compositional changes of the SiC surface. Surface enrichment in silicon [3, 4, 5], restored stoichiometry [6, 7] and also carbon enriched surfaces [8, 9] after sputtering with argon were reported. These discrepancies strongly motivate evaluation of the measured data in order to get a detailed picture of the silicon carbide surface after sputtering.

2 EXPERIMENTAL

All experiments were conducted on n-type 6H-SiC single crystal substrates with a smooth surface (rms= 0.5 nm). The samples were transferred without any pretreatment into the UHV chamber of the Riber ASC 2000 Auger electron spectrometer. During Auger measurement, the chamber pressure was 10^{-7} Pa. First, the sample surface was sputtered with argon ions of x keV ($x = 1$, 2 and 4) under an incidence angle of 80° with respect to surface normal until the steady state was reached. Afterwards, the ion gun was adjusted down to the value of 300 eV. This procedure took approximately 5 minutes. Then, Auger depth profiling was carried out of the pre-bombarded surface in a sequential mode, *ie*, by alternating signal measurement and sputtering. The incidence angle of the ion beam was not changed. The current density of the ion beam was $3.65\,\mu\text{A/cm}^2$ and was constant during the whole experiment. Pre-bombardment with the keV ion beam was carried out with current density equal to $7.3\,\mu\text{A/cm}^2$. The following spectra were recorded with 0.5 eV energy steps: silicon LVV and KLL transitions at 92 and 1615 eV, respectively, and carbon at 272 eV. The oxygen spectra at 512 eV were recorded with 1 eV energy steps. The electron gun was directed perpendicularly to the sample surface and operated at 3 keV energy of the primary beam with spot diameter

[*] Center for Micro- and Nanotechnologies, TU Ilmenau, Gustav-Kirchhoff-Str. 7, D-98693 Ilmenau, Germany
[**] Department of Microelectronics, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

ISSN 1335-3632 © 2003 FEI STU

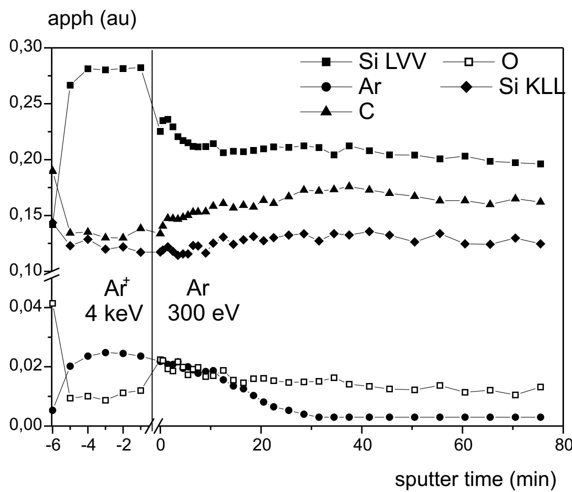

Fig. 1. Auger depth profile of an altered layer at a silicon carbide surface obtained by 300 eV argon sputtering. The altered layer was created by pre-bombardment with 4 keV argon ions. The sputtering with 300 eV ions started at time zero.

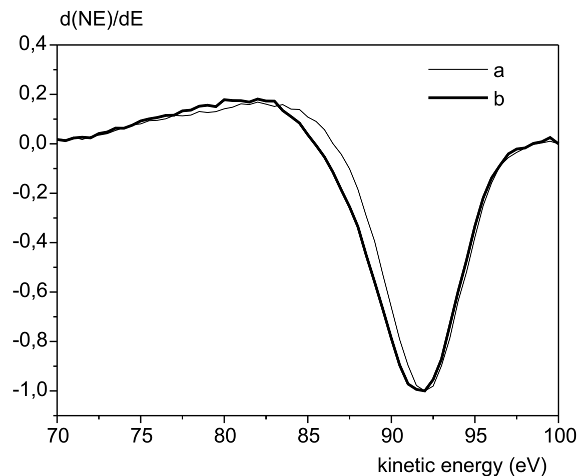

Fig. 2. Derivative Si LVV Auger spectra recorded at the SiC surface after bombardment with 4 keV Ar ions (a) and after exposure to the residual atmosphere in the UHV chamber (b).

$10\,\mu$m, the electron beam current was $1\,\mu$A. The signal from the sample was recorded in differential mode with a CMA analyzer (the electron gun was placed co-axially) working with energy resolution 0.3 %. The take off angle of CMA was 42° with respect to the surface normal.

3 RESULTS AND DISCUSSION

In order to produce an altered layer, the surface of the 6H SiC single crystal was bombarded with argon ions of energies from 1 to 4 keV. The constant silicon-to-carbon Auger signal ratio with prolonged ion bombardment served as the indicator for the steady state. After the steady state was reached, the sputter depth profiling procedures were carried out through these altered layers by means of AES. For the sputter depth profiling procedure, the energy of the ion beam was reduced to 300 eV in order to keep the distorted depth small enough in comparison with that from the preceding bombardment. Figure 1 presents the Auger depth profile measured on the silicon carbide single crystal pre-bombarded with 4 keV argon ions. Here, the Auger peak-to-peak heights (I_{pph}) are displayed as a measure for the Auger signal. Replacement of the Auger signal by the peak height is acceptable for quantification in such cases only, if the shape of the Auger peak is not affected by the chemical state of the investigated sample [10]. In our experiments, however, we did not observe any changes in the peak shape of both silicon and carbon Auger transitions. The obvious reduction of the silicon signal occurring during ion gun adjustment was attributed to the adsorption of oxygen from the residual atmosphere. Due to the Si-O bonds at the surface, the silicon Auger peak became broader and its height decreased. A well established and reliable quantification tool in the case of peak shape changes in AES is factor analysis [11]. In factor analysis, the whole series of spectra are evaluated, so that the peak shape changes can be taken into account.

Factor analysis has often been applied to evaluate AES depth profiles [12–16]. The main precondition for applying factor analysis to evaluate spectroscopic data is the assumption that all spectra can be described by a linear combination of a low number of basic spectra. The evaluation procedure consists of two main parts. In the first part, the principal component analysis (PCA) determines the number of basic spectra as well as the basic spectra themselves needed for sufficient reproduction of the whole spectra set. In the second part, the basic spectra obtained from the principal component analysis, which have an abstract form, are transformed into spectra with a physical meaning. The transformation can be performed either by means of target testing or rotation of the basic spectra. Details of these procedures can be found in [11]. Let us shortly introduce the idea of factor analysis. The data matrix **D** is composed from the measured spectra. The spectra are introduced as column vectors. The dimension of **D** matrix is $m \times n$, m is the number of measured points in a single spectrum and n is the number of the spectra within the depth profile. Then the data matrix is decomposed as

$$D_{m,n} = R_{m,n} \cdot C_{n,n} \,. \tag{1}$$

The columns of the **R** matrix represent n basic spectra, the rows of the **C** matrix contain the weighting factors, the so-called loadings for respective basic spectra. Decomposition procedure is based on the linear least square method so that the basic spectra are ordered with their importance in the **R** matrix. The first columns of the **R** matrix contain basic spectra reflecting the useful signal, the last columns are connected with the noise in the

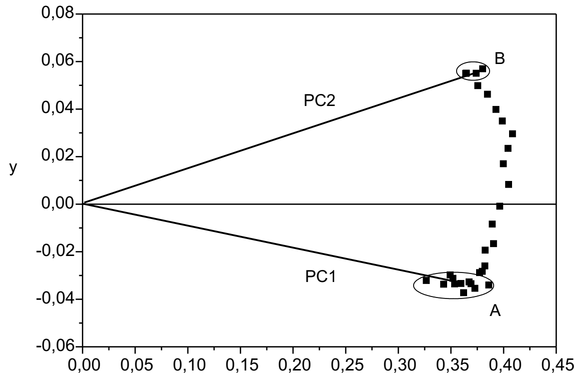

Fig. 3. Projection of the carbon spectra recorded during sputter depth profiling of the silicon carbide pre-bombarded with 4 keV Ar^+ ions onto the factor space as determined from the principal component analysis. The spectra from the beginning of the depth profile are projected in region A, the spectra from the end of the depth profile are projected in region B.

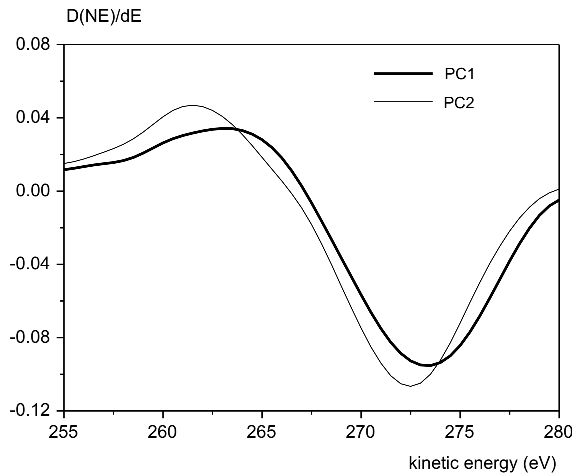

Fig. 4. Spectroscopic form of the principal components PC1 (A) and PC2 (B) as displayed in Fig. 3.

measured spectra. The number of basic spectra can be reduced and Eq. 1 can be rewritten as

$$D_{m,n} = R_{m,k} \cdot C_{k,n} + E_{m,n} \,, \qquad (2)$$

where **E** is a matrix representing the noise in the measured spectra, k is the number of the basic spectra necessary for sufficient reproduction of the data matrix. Malinowski [11] and Pieterwas *et al* [17] proposed some methods and empirical functions how to determine the number of basic components (spectra). The basic spectra in matrix **R** build the so-called factor space. They are orthogonal and have an abstract form. In order to get useful information, a new basis of the factor space should be found. Either the assumed spectra are tested, if they lie within the factor space, or the basic spectra are rotated within the factor space and are compared with other spectra.

Due to its small information depth and thus the high surface sensitivity, the silicon LVV transition would be the most appropriate for the factor analysis. The information depth can be calculated as $3Q\lambda(E)\cos(\alpha)$, where λ is the inelastic mean free path of electrons with energy E in the solid, α is the take off angle of the analyzer, and Q is the correction factor due to the elastic scattering of electrons (~ 0.8). Using the TPP-2M formula for the calculation of the inelastic mean free paths in SiC [18] we get the information depths of 0.95 nm and 1.6 nm for silicon LVV and carbon Auger transitions, respectively. Nevertheless, we decided not to use the silicon peak for factor analysis. It is apparent that the Si LVV signal $I_p ph$(Si) decreased during switching the ion energy down to 300 eV (Fig. 1), whereas carbon and silicon KLL signals did not change. There was a small oxygen signal present in the spectra after pre-bombardment with a keV argon ion beam. The oxygen signal became twice higher within the time of ion gun adjustment and decreased only slightly with prolonged sputtering by 300 eV argon ions. It is known that oxygen is bond preferentially to silicon atoms at SiC surfaces [19–21]. The LVV transitions involve the valence band and therefore their peak shapes are very sensitive to the chemical environment of respective species in the solid. There were only minor differences in the carbon peak shape (core-valence-valence transition) after surface exposure to the residual atmosphere, whereas a slight peak shift and peak broadening of 0.8 eV could be observed for the silicon LVV peak (Fig. 2). The peak broadening in the lower energy direction indicates creation of Si-O bonds at the surface. Thus, in the following we will concentrate on the carbon Auger signal due to its insensitivity to oxygen. The silicon KLL transition due to its great information depth (5.8 nm) and the low energy resolution of the analyzer at such high energies (1615 eV) was not taken into account for quantification.

As the first attempt, the principal component analysis was carried out on a set of carbon Auger spectra without any data pre-treatment. It resulted in three principal components needed for the reproduction of the data matrix. Target testing made with a constant spectrum as a test vector showed that one of these three components could be described by a constant. Thus, after subtraction of a constant part from all Auger spectra prior to PCA, the number of principal components in the data matrix could be reduced to two. The spectra were measured in a narrow energy window, therefore it was not possible to determine the constant part of the particular spectra from the high energy side of the spectra as proposed by Baunack [22]. However, subtraction of a unique constant spectrum from all carbon Auger spectra led also to the reduction of the number of principal components. The number of principal components was determined by an indicator function and imbedded error function [11] as well as by visual inspection of the residual spectra. The background due to inelastically backscattered primary electrons and

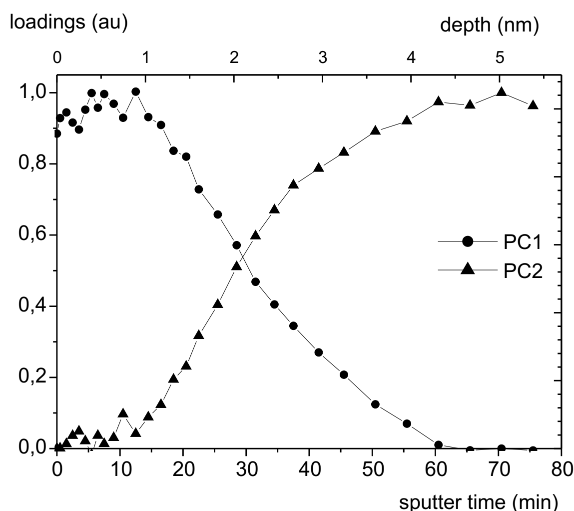

Fig. 5. Depth profiles of the principal components PC1 and PC2 of a 4 keV pre-bombarded silicon carbide sample obtained by 300 eV sputtering (Ar, 80°).

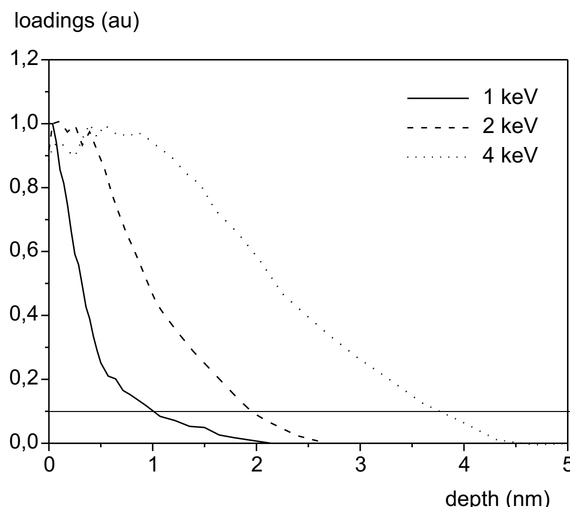

Fig. 6. Set of the depth profiles of the principal component PC1 (standing for the altered layer) for 1, 2 and 4 keV bombardment by Ar ions under 80°.

secondary electrons, which can be roughly described by a linear function in the measured energy window, is the origin for the constant part in the differentiated spectra.

Figure 3 presents the projection of the measured carbon spectra onto the factor space determined by PCA of the set of carbon spectra after constant subtraction. The factor space is determined by the first two basic spectra in the **R** matrix, these being orthogonal. Spectra from the beginning of the depth profile are projected in region A, spectra from the end of the depth profile are projected in region B of Fig. 3. Thus, the measured depth profile shows a transition from one state of carbon at the surface to another state of carbon in the depth. The original state is represented by vector PC1 (principal component) and the final state by PC2. The principal components are displayed in their spectroscopic form in Fig. 4. They were calculated by rotation of the basic spectra. The shape of the curve between A and B indicates that the sum of the loadings is not everywhere equal to one. Otherwise the points would lie on a straight line. The graphical presentation of the factor space can be transcribed into a depth profile of the two principal components. In Fig. 5 the loadings (weighting factors) of the PC1 and PC2 for appropriate spectra are displayed as a function of the sputtering time. In order to transform the time axes into depth, the sputtering rate was measured. The surface of the SiC single crystal was partly covered by an Al foil. Then, the surface was sputtered along the foil edge in order to create a sputter crater. After sputtering, the crater edge was measured with AFM. From the achieved depth (80 nm), sputtering time and ion current density, the sputtering yield of 0.49 atoms/ion was calculated. With the help of the measured sputter rate, the time axes could be transformed into the depth scale (upper axis in Fig. 5).

The same procedure as for 4 keV pre-sputtering was carried out for the depth profiles obtained from the surfaces pre-bombarded with 1 and 2 keV ions. For all measurements, two components were necessary to reproduce the measured matrix of the carbon spectra. The depth profiles of the principal components referring to carbon at the pre- sputtered surface are summarized in Fig. 6. The region within the SiC sample, which refers to the carbon state at the pre sputtered surface, exceeds deeper into the sample with increasing energy. At the beginning of the depth profiles in Fig. 6, there are plateaus with widths of approximately 0.4 and 0.95 nm for 2 and 4 keV pre-sputtered surfaces, respectively. For 1 keV, no plateau exists at the beginning of the depth profile. Then, transition regions follow. The widths of these regions calculated as the 90 %–10 % decrease are 0.9, 1.45 and 2.6 nm for 1, 2 and 4 keV, respectively. Finally, the depth of the altered layers measured as the drop of the signal down to 10 % are 1.00, 1.95 and 3.8 nm for 1, 2 and 4 keV, respectively.

4 CONCLUSIONS

The thickness of the layer altered by ion bombardment of single crystalline SiC with 1 to 4 keV Ar ions under 80° were determined by means of low ion energy Auger depth profiling. Factor analysis of the carbon Auger peak was applied for identification of the damaged region. The thicknesses of the altered layers measured as the drop of the signal down to 10 % were 1.00, 1.95 and 3.8 nm for 1, 2 and 4 keV, respectively.

Acknowledgement

The work is supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic under No. 1/8180/01 and Nem/Slov/1.

References

[1] BUSSING, T. D.—HOLLOWAY, P. H.—WANG, Y. X.—MOULDER, J. F.—HAMMOND, J. S.: J. Vac. Sci. Technol. B **6** (1988), 1514.

[2] CAO, Z.—OECHSNER, H.: Nucl. Instr. And Meth. B **168** (2000), 192.

[3] BELLINA Jr., J. J.—FERRANTE, J.—ZELLER, M. V.: J. Vac. Sci. Technol. A **4** (1986), 1692.

[4] JORGENSEN, B.—MORGEN, P.: Surf. Interface Anal. **16** (1990), 199.

[5] OSWALD, S.—WIRTH, H.: Surf. Interface. Anal. **27** (1999), 136.

[6] LEE, W.-Y.: J. Appl. Phys. **51** (1980), 3365..

[7] MUEHLHOFF, L.—CHOKE, W. J.—BOZACK, M. J.—YATES Jr., J. T.: J. Appl. Phys. **60** (1986), 2842.

[8] PEZOLDT, J.—STOTTKO, B.—KUPRIS, G.—ECKE, G.: Mat. Sci. Eng. B **29** (1995), 94.

[9] BECK, H. L.—LEE, M.-H.—OHUCHI, F. S.: Mat. Res. Soc. Symp. Proc. **438** (1997), 253.

[10] LIDAY, J.—HOFMANN, S.—HARMAN, R.: Vacuum **43** (1992), 339.

[11] MALINOWSKI, E. R.: Factor Analysis in Chemistry, 3rd Ed., John Wiley and Sons, Inc., New York, 2002.

[12] BUBERT, H.—MUCHA, A.: Surf. Interface Anal. **19** (1992), 187.

[13] SARKAR, M.—CALLIARI, L.—GONZO, L.—MARCHETTI, F.: Surf. Interface Anal. **20** (1993), 60.

[14] CHEMELLI, C.: Surf. Interface Anal. **22** (1994), 60.

[15] MOROHASHI, T.—HOSHI, T.—NIKAIDO, H.—KUDO, M.: J. Vac. Sci. Technol. A **16** (1998), 2257.

[16] SANZ, J. M.—PRIETO, P.—QUIROS, C. ELIZALDE, E.—FERNANDEZ, A.—PEREZ-CASERO, R.: Surf. Interface Anal. **26** (1998), 806.

[17] Pieterwas, R.—Ecke, G.—Kosiba, R.—RÖßLER, H.: Fresenius J. Anal. Chem. **368** (2000), 326.

[18] TANUMA, S.—POWELL, C. J.—PENN, D. R.: Surf. Interface Anal. **21** (1993), 165.

[19] KAPLAN, R. J. Appl. Phys. .

[20] MIZOKAWA, Y.—GEIB, K. M.—WILMSEN, C. W.: J. Vac. Sci. Technol. A **4** (1986), 1696.

[21] JORGENSEN, B.—MORGEN, P.: J. Vac. Sci. Technol. A **4** (1986), 1701.

[22] BAUNACK, S.: Microchimica Acta **133** (2000), 307.

Received 12 December 2002

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.

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.

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.

Oliver Ambacher (Prof, Dr) was born 1963 in Welmerskirchen, Germany. He graduated in physics at the LMU Munich in 1989 and received his PhD in physics from the TU Munich in 1993. Since 2002 he has been professor of the Department of Nanotechnology at the TU Ilmenau. His teaching and research activities cover nanotechnology, nanoanalytics and nanodiagnostics as well as technology of devices based on Group III nitrides.

EXPORT - IMPORT
of ***periodicals*** and of non-periodically
printed matters, ***books*** and ***CD - ROMs***

Krupinská 4 PO BOX 152, 852 99 Bratislava 5,Slovakia
tel.: ++421 2 638 39 472-3, *fax.:* ++421 2 63 839 485
e-mail: gtg@internet.sk, http://www.slovart-gtg.sk