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COMMUNICATIONS

AUGER ELECTRON SPECTROSCOPY OF SILICON CARBIDE

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The paper is devoted to evaluating the concentration of silicon on the surface of SiC exposed to bombardment by Ar^+ ions. For quantitative interpretation of the measured Auger spectra, the method was used in which the Auger current is determined as the area below the Auger peak in the direct $N(E)$ spectrum after subtracting the background of inelastically scattered Auger electrons of the given peak and of the so-called true secondary electrons. We have found that bombardment of SiC by Ar^+ ions with energy 1 keV at an angle of 68° with respect to the surface normal and with the sample rotating at 6 rpm leads to Si depletion of SiC in comparison with its stoichiometric composition. The retrieved concentration of Si was $35.4\,\text{at/nm}^3$ in the case of using the Si LVV spectra, and $39.7\,\text{at/nm}^3$ if Si KLL spectra were used.

K e y w o r d s: AES, quantitative analysis, sputtering, SiC, AES depth profiling

1 INTRODUCTION

SiC became an important material for high-frequency and high-power electronics. Even though it has been investigated by diverse surface sensitive analytical techniques such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) for more than twenty years, some of its properties still have not been understood satisfactorily or some results appear to be contradictory. For instance, as far as alterations are concerned in elemental composition of the surface due to bombardment by noble gas ions, which is a standard procedure in native oxide removal or in depth profiling, numerous papers have been published reporting different results: Si enrichment of the surface [1, 2, 10, 11], stoichiometric SiC surface [6, 8, 9, 12, 13], and even surface enrichment by carbon [3–7, 9]. Therefore the issues of the bombardment of SiC by high-energy noble gas ions require further extensive studies mainly from the point of view of the reliability of quantitative analysis.

In quantitative AES, Auger signals are obtained from both direct electron energy spectra and electronically or numerically differentiated electron energy spectra. In dependence on the type of spectrum, the Auger signal representing the value of the Auger current is defined in different ways. The most accurate method of determining the Auger current is based on evaluating the area below the Auger peak in the direct spectrum. This is performed after subtracting the background, which may lead to considerable problems in the case of complicated, mainly low-energy Auger peaks. The topic of the present work is to establish the actual effect of ion bombardment upon the composition of the surface of SiC by quantitative AES.

2 EXPERIMENTAL

The depth profile of a SiC/Si heterostructure with a 95 nm thick SiC layer was measured in a VG Microlab Auger electron spectrometer. The energy of the primary electron beam was 10 keV, the beam current was 70 nA. The electron beam struck the surface perpendicularly. The energy spectra of the emitted electrons were recorded by a hemispherical analyzer with 0.05 % energy resolution. The angle of the analyzer with respect to the surface normal was 60°. Depth profiling was conducted in a sequential mode, *ie*, alternating ion beam sputtering and analysis using a primary electron beam. The energy of Ar^+ ions was 1 keV, the total current over the whole sample being $1.6\,\mu$A. The ion beam struck the sample at an angle of 68° with respect to the surface normal and was scanned over an area of approx. $3\,\text{mm}^2$. During sputtering, the probe rotated at 6 rpm. The spectra discussed in this paper were taken from a depth of approx. 10 nm from the SiC/Si interface for silicon carbide, and from the substrate for silicon.

3 RESULTS AND DISCUSSION

a) Quantitative analysis using Si LVV transition

To calculate the concentration of silicon, the approach of Jorgensen and Morgen [3] was used. They interpreted their Auger spectra of SiC making use of elemental references (Si and C). Their approach can be expressed as

$$\frac{I_{Si}^{SCi}}{I_{Si}^{Si}} = \frac{N_{Si}^{SiC}}{N_{Si}} \frac{[1 + r_{SiC}(E)]\,\lambda_{SiC}(E)}{[1 + r_{Si}(E)]\,\lambda_{Si}(E)}\,, \tag{1}$$

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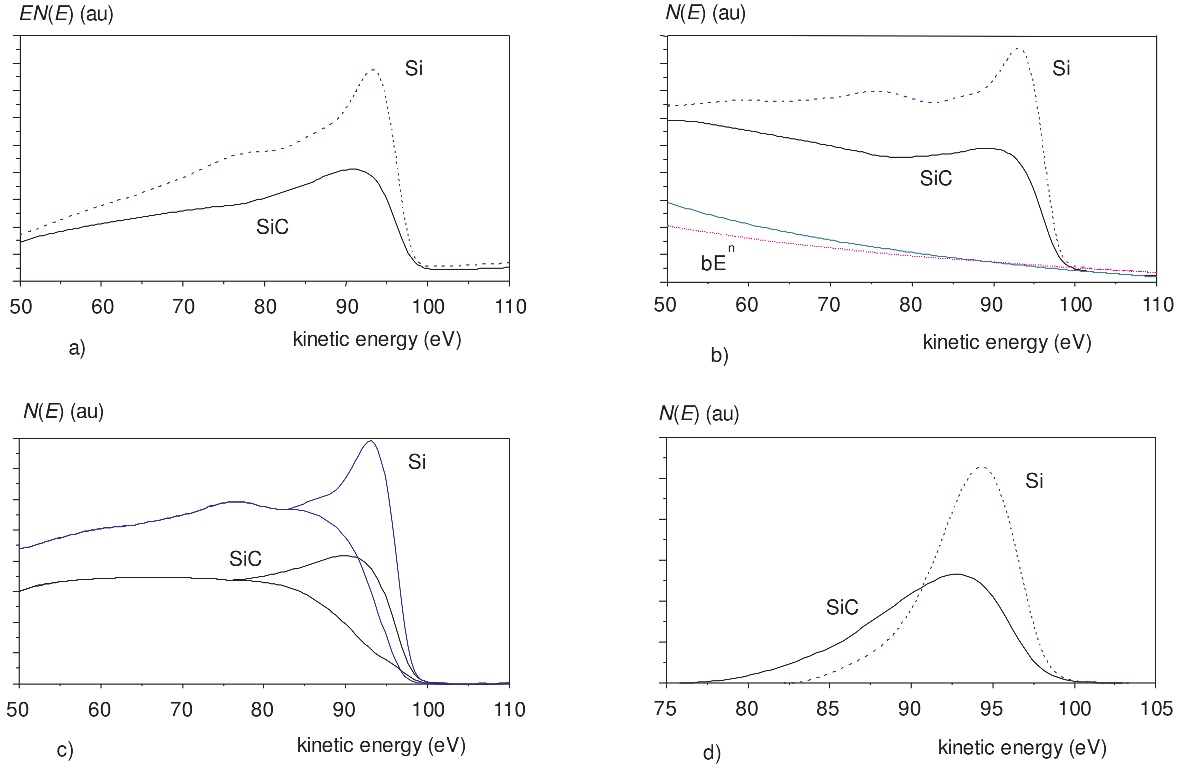

Fig. 1. Auger electron spectrum of Si LVV taken from the silicon substrate after complete removal of the SiC layer and from SiC in a depth of approximately 10 nm in front of the SiC/Si interface:
a) direct, as measured spectrum $EN(E)$,
b) in the form $N(E)$ obtained by dividing the direct $EN(E)$ spectrum by E; in the lower part of the figure, distribution curves of the true secondary electrons in the Auger spectra of Si and SiC are shown obtained by approximating the extrapolated background curves by bE^{-n},
c) after subtraction of the background of true secondary electrons from Fig. 1b, and with the background of inelastically scattered Auger electrons determined after the method of Shirley [16],
d) after correction of the background of inelastically scattered Auger electrons from Fig. 1c.

where I^{Si}, I^{SiC} are the Auger electron currents from silicon in Si and SiC, respectively, $N_{Si}(= 49\,\mathrm{at\,nm^{-3}})$ is the atomic density of silicon, and $N_{SiC}(= 48\,\mathrm{at\,nm^{-3}})$ is the atomic density of silicon in SiC. The attenuation lengths λ_{Si} and λ_{SiC} were evaluated for energy 90 eV (LVV transition of Si) according to [14]

$$\frac{\lambda(E)}{\lambda_i E} = \left(1 - 0.028Z^{0.5}\right)[0.501 + 0.0681\ln(E)]\,, \qquad (2)$$

where $\lambda_i(E)$ is the inelastic mean free path of electrons. To calculate $\lambda_i(E)$, TPP-2M equation [15] is used

$$\lambda_i(E) = \frac{E}{E_p^2[\beta\ln(\gamma E) - (C/E) + (D/E^2)]} \qquad (3)$$

where

$$\beta = -0.1 + 0.944\left(E_p^2 + E_g^2\right)^{1/2} + 0.069\rho^{0.1}\,, \qquad (3a)$$

$$\gamma = 0.191\rho^{-0.5}\,, \qquad (3b)$$

$$C = 1.97 - 0.91U\,, \qquad (3c)$$

$$D = 53.4 - 20.8U\,, \qquad (3d)$$

$$U = N_V\rho/M = E_p^2/829.4\,, \qquad (3e)$$

$$E_p = 28.8(N_V\rho/M)^{1/2}\,, \qquad (3f)$$

where λ_i is the inelastic mean free path [Å], ρ is the density [g/cm^3], N_V is the number of valence electrons, M is the molecular weight, E_g is the bandgap energy [eV] and E_p is the free-electron plasmon energy. Using $N_V = 4$ (for both materials, Si and SiC), and $\rho_{Si} = 2.3\,\mathrm{g/cm^3}$, $\rho_{SiC} = 3.3\,\mathrm{g/cm^3}$, $M_{Si} = 28$ and $M_{SiC} = 20$ one obtains $\lambda_{Si}(90\,\mathrm{eV}) = 0.37$ nm and $\lambda_{SiC}(90\,\mathrm{eV}) = 0.40$ nm.

Since the spectra of Si in SiC come from a layer of SiC with a thickness as small as approx. 10 nm, the effect of backscattering factors upon the quantification of Auger data is ruled out. The atomic density of silicon in SiC, as evaluated from LVV Auger peaks, can be expressed as

$$N_{Si}^{SiC} = 0.925\,N_{Si}^{Si}\frac{I_{Si}^{SiC}}{I_{Si}^{Si}}\,. \qquad (4)$$

The peaks of Auger electrons of Si in SiC (taken from a depth of approx. 10 nm in front of the SiC/Si interface) and from Si (taken from the Si substrate after complete sputter removal of the SiC layer) in the as measured form,

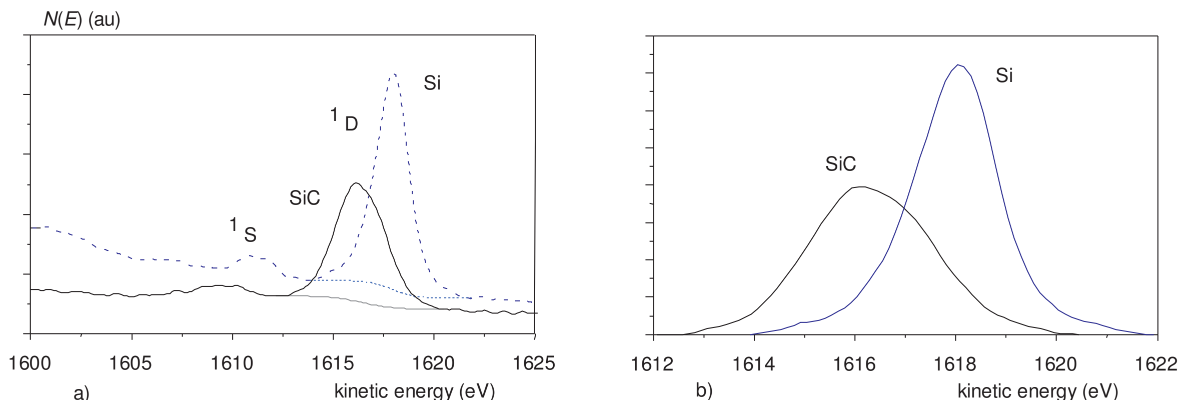

Fig. 2. Si KLL Auger spectra of Si and SiC:
a) in the form of $N(E)$,
b) /after correction of the background of inelastically scattered Auger electrons according to the method of Shirley [16].

thus $EN(E)$ are shown in Fig. 1a. Quantitative interpretation can be made on both direct, as-measured spectra and on spectra obtained after subtracting the background. Beforehand, the spectra have to be recalculated into the $N(E)$ form. This procedure consisted in dividing the direct spectra $EN(E)$ (Fig. 1a) by E (Fig. 1b). By subtracting the background, one obtains the actual Auger spectra. The integral of the peak in this spectrum represents the Auger current. The background in Auger spectra is composed of three contributions: the so-called true secondary electrons, inelastically scattered primary electrons, and inelastically scattered Auger electrons. The second aforementioned contribution is negligible in the energy range around 100 eV. The spectrum of true secondaries can be replaced, fitted by a curve bE^{-n}. Figure 1b shows the spectra of secondary electrons in Auger spectra of silicon measured on Si and on SiC. The fitting procedure of subtracting the background was performed on the high-energy sides of the spectra. After subtracting the background corresponding to the cascades of true secondary electrons from the measured spectra one obtains the Si LVV Auger spectra from Si and SiC (Fig. 1c). These consist of the original, actual Auger spectra of silicon from SiC and Si and of a contribution from inelastically scattered Auger electrons of silicon.

Subtraction of the background resulting from inelastically scattered Auger electrons is even more difficult than in the case of the background of secondary electrons, in particular in the low-energy region ($\approx$ 100 eV). One of the possible methods is that of Shirley [16, 17]. Figure 1c shows the background correction after Shirley applied to spectra corrected for secondary electrons. The resulting spectra are shown in Fig. 1d. These spectra show the actual Si LVV Auger peaks for silicon and for SiC. From the areas below these spectra one obtains silicon-depleted surfaces with concentration $35.4\,\mathrm{at/nm}^3$.

b) Quantitative analysis using Si KLL transition

For quantification based on the use of the KLL peak, the attenuation length must be calculated anew. From equation (2) and by using TPP-2M formula for $\lambda_i(E)$ calculation, for energy 1615 eV one obtains the following values of the attenuation lengths:

$\lambda_{Si}(1615\,\mathrm{eV}) = 3.2$ nm,
$\lambda_{SiC}(1615\,\mathrm{eV}) = 3.0$ nm.

Then, equation (3) for the KLL transition can be written as

$$N_{Si}^{SiC} = 1.07\, N_{Si}^{Si} \frac{I_{Si}^{SiC}}{I_{Si}^{Si}}\,. \tag{5}$$

Figure 2a shows the Si KLL Auger spectra of Si and SiC in the form $N(E)$ after dividing the measured $EN(E)$ spectra by energy E. The high energy resolving power of the analyzer allows measuring the Auger peaks very accurately. In this way one can resolve the ^{1}S transition from the main $KL_{2,3}L_{2,3}$ ^{1}D peak. For quantitative analysis, the main transition is used and discussed. These spectra are evaluated in a similar way like the LVV peaks, with distinction that the background in $N(E)$ spectra was established only by Shirley's method (Fig. 2a). The resulting spectra are shown in Fig. 2b. The evaluation of peak areas after background subtraction results in concentration $39.7\,\mathrm{at/nm}^3$, thus in a Si depleted surface, as compared with a single crystalline material free of defects and adsorbate. This result is in agreement with that of evaluation of the Si LVV peaks.

4 CONCLUSIONS

Quantitative evaluation of Si LVV and KLL Auger spectra has shown that bombardment of the surface of SiC by Ar ions with energy 1 keV at an angle of 68° with respect to the surface normal, while the sample rotates at 6 rpm, leads to silicon depletion of the surface as compared with its stoichiometric composition. The measurements have shown that the evaluation of the peak areas below the Auger peak in the direct $N(E)$ spectrum after subtraction of the so-called true secondary electrons (Si LVV) and inelastically scattered Auger electrons (Si LVV, Si KLL) leads to Si concentration $35.4\,\mathrm{at/nm}^3$

in the case of using the Si LVV spectra, and 39.7 at/nm^3 if Si KLL spectra are used.

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