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Determination of the thickness distribution of a graphene layer grown on a 2" SiC wafer by means of Auger Electron Spectroscopy depth profiling

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Abstract

Auger electron spectroscopy (AES) depth profiling was applied for determination of the thickness of a macroscopic size graphene sheet grown on 2 inch 6H-SiC (0001) by sublimation epitaxy. The measured depth profile deviated from the expected exponential form showing the presence of an additional, buffer layer. The measured depth profile was compared to the simulated one which allowed the derivation of the thicknesses of the graphene and buffer layers and the Si concentration of buffer layer. It has been shown that the C made buffer layer contains about 30% unsaturated Si. The depth profiling was

carried out in several points (diameter $50\mu m$), which permitted the constructing of a thickness distribution characterizing the uniformity of the graphene sheet.

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1. Introduction

Graphene, because of its exceptional features has probably been the most investigated material in recent years. Practically all possible experimental methods have been applied to characterize its geometrical, electronic, thermal, etc., properties. The most basic types of experimental methods applied for graphene research are those with atomic resolution, like scanning tunneling, atomic force and transmission electron microscopies. Though these methods provide the most exact characterization of graphene they cannot be used to characterize a macroscopic size graphene sheet. Thus, the increase of the real industrial scale production of graphene based either on CVD or by sublimation epitaxy on silicon carbide (SiC) prompted new efforts to develop methodologies which are able to characterize the average thickness, defect density etc. of graphene having wafer size typically used in semiconductor industry. If we restrict ourselves only to the measurement of the average thickness of graphene still many methods can be used; a relatively large selection of possible measurements is discussed in ref [1]. Among the known methods Raman spectroscopy is the most applicable one since it a./ can verify the presence of graphene, b./ measures the defects, c./ can be applied to determine the thickness, and as an optical method provides a simple measurement. However, while it is excellent for graphene flakes, it's application is more complicated for the cases when graphene is on substrates like SiC or metal, which on the other hand are perspective materials for graphene production. Ellipsometry mapping was also applied for measuring the thickness of the graphene layer produced by sublimation epitaxy on silicon carbide [2]. The signal measured by ellipsometry depends on the thickness and the optical constants of the layer and thus, the thickness cannot be directly determined. X-ray

diffraction has been also used to determine the thickness distribution of graphene layer [3]; this method needs high energy X-ray facility, however. It is interesting that Auger electron spectroscopy (AES), the classical surface sensitive analytical tool, has been rarely used in graphene research. The main reason might be that though the shape of the carbon Auger peak of graphene is strongly different from that of various carbides it is only slightly different from the various graphite forms [1]; thus, the identification of graphene is not completely safe by using AES. On the other hand AES [1,4] as well as X-ray photoelectron spectroscopy (XPS) [5] can be readily applied for the determination of thickness of the graphene layer since the transport (attenuation) of medium energy electrons through ad-layers is well known [6]. Xu et al. [1] proposed AES as A Rational Method for Determining Thickness of Graphene Films. In the mentioned applications [1,4] the ratio of carbon and substrate Auger intensities had been measured and compared with the calculated ones. The accuracy and sensitivity of the procedure depend on the sensitivity of the measured ratio on the layer thickness. Fortunately all perspective substrates (Cu, Ni, SiC, SiO₂) for graphene production emit low and high energy Auger electrons of the same elements. The attenuation lengths of the low and high energy Auger electrons in graphene are 0.4-0.8 nm and 3 nm-4 nm, respectively. Thus, applying low energy signal electrons for the measurement high and low accuracy can be obtained for thin layers (up to 2-3 graphene layers) and for more (4-6) graphene layers, respectively. On the other hand, using the high energy signal electrons the attenuation is relatively weak; the accuracy is poor and good in less than 3 and more than 3 graphene layers, respectively. Therefore the method can be applied for a wide range numbers of graphene layers. Its shortcomings are a./ the single measured ratio might result is a large error, b./

in case of SiC substrate the measured Si signal originates from the pristine substrate and the buffer (interface) layer, that is, we have two unknown and one equation. Here we will show an appropriate use of AES depth profiling for determination the average thickness of the graphene layers on any substrate. AES depth profiling is a classical extension of AES for thin film analysis. Performing sequential AES measurement and sputter removal steps results in Auger intensities vs. sputtering time curve from which the concentration distribution along the depth can be reconstructed. Since the AES is capable to collect signals from several points, and the large area uniform layer removal is possible, thus several in-depth distributions can be recorded parallel. The procedure thus starts with a first measurement like those performed in [1,4,5], but is continued by several additional AES analysis resulting in the depth profile, that is, in several Auger intensities vs. thickness values, which strongly improves the accuracy of the method. As a case study we will apply the AES depth profiling to measure the average thickness of a graphene layer on the surface of SiC. This is in fact a complicated test case due to the presence of the buffer layer on the surface of SiC, but we will show for the first time that Auger depth profiling can determine both the thicknesses of graphene and the buffer layer reasonably well.

2. Experimental details

The graphene layers were prepared on the Si-terminated face of 0001 oriented 6H-SiC single crystal wafer of 2 inch size by high temperature sublimation process [7] developed at Linköping University. While growth on 6x12 mm² area resulted in one monolayer (1ML) graphene as demonstrated in [7], the same growth conditions did not sustain the

same thickness homogeneity on the 2 inch SiC wafer. This is due to the presence of structural defects, e.g. micropipes, and wafer bending typical for large area SiC wafers, as well as surface scratches related to the wafer surface polishing. Although not typical, we considered this sample as exemplary for this particular study in which the potential of Auger depth profiling to distinguish between different graphene thicknesses will be validated.

STAIB DESA 150 pre-retarded cylindrical mirror analyzer (CMA) working in electron counting mode was applied to collect the spectra for AES. The analyzed area is determined by the shape of the exciting electron beam (10 nA); it is circular with a diameter of 50 μ m.

Our standard depth profiling technique, that is, sequential AES analysis and ion removal steps were applied [8]. The sputtering conditions were as follows: projectile Ar^+ , energy 0.5 keV, angle of incidence (with respect to the surface normal) 80°, specimen rotation (2 rpm). Using such ion bombardment conditions the disadvantageous ion bombardment induced roughening and ion mixing are strongly reduced [9], and depth resolution in the range of some nm can be achieved.

2. 1. Determination of the graphene layer thickness.

The number of Auger electrons is proportional to the number of excited atoms, which makes possible the chemical analysis. The number of detected Auger electrons is the integral of Auger electrons emitted at various depths and thus attenuated variously. This integral in general case cannot be inverted and the concentration distribution providing the measured Auger intensities cannot be directly determined. On the other hand the

transport of electrons in the solid is known reasonably well [6]. Based on this we can calculate the intensity of Auger electrons emitted by any distribution of an element, which allow us to determine concentration in-depth distribution. The procedure is as follows. An initial sample structure (concentrations in-depth distributions) is assumed and the Auger electron intensities are calculated. Then we remove a thin layer from the surface and calculate the Auger electron intensities again. The simulated depth profile is obtained by repeating these steps as long as desired (until the ad-layer is removed). The simulated depth profile is to be compared with the measured one and the initial structure is varied until a good agreement is reached. For this procedure the Auger intensities as well as the sputtering process should be simulated [10].

2.1.1. Calculation of the Auger electron intensities.

The Auger electron intensities are calculated by using the standard approach which assumes that the attenuation of the signal electron is caused by the inelastic [6] and elastic interactions with the materials in which it travels. This approach results in the electron effective-attenuation-length (EAL), which can be calculated based on ref 11. For the calculation of the AES intensities of the graphene covered SiC we will suppose a structure shown in Fig. 1.

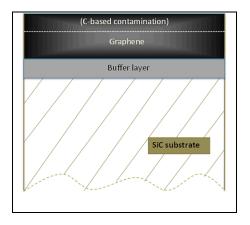


Figure 1. The assumed structure.

Beside the graphene the sample might consist of some C contamination on its surface and a buffer layer between the pristine SiC and graphene, which is rich in carbon [12] and has a similar structure as the graphene [13]. Thus, the Auger electron emitted by the SiC substrate is attenuated by these three layers, and the signal reaching the detector is proportional to

$$I_{SiC} * exp(-d_b/\lambda_b) * exp(-d_{gr}/\lambda_{gr}) * exp(-d_C/\lambda_C)$$
(1)

where I_{SiC} is the intensity of the Si_{LVV} and/or Si_{KLL} Auger electrons emitted from the pure SiC sample, λ -s are the corresponding EAL-s for the Auger electrons traveling in material shown by the indexes of $_{b, gr, C}$ which stand for buffer, graphene and C contamination, respectively, $d_{b, gr, C}$ are the corresponding layer thicknesses. The same quantity for the buffer layer is as follow:

$$I_{SiC}N_b/N_{SiC}\lambda_b/\lambda_{SiC}X_b/X_{SiC}(1-exp(-d_b/\lambda_b)) * exp(-d_{gr}/\lambda_{gr}) * exp(-d_C/\lambda_C)$$
(2)

where *N* and *X* are the densities and concentrations of Si in the layer given by the index, respectively. The counts measured by the detector are the sum of these two components; both vary during depth profiling since the thicknesses (*d*) of the layers vary. The EALs are well defined for pure materials; in our case in graphene (the corresponding inelastic mean free path (IMFP) was taken from ref 1). To obtain the EAL for the buffer layer we use the approximation that the scattering cross sections are added, that is, $1/\lambda = \sum X_i/\lambda_i$. The EAL-s have been obtained from Powell et al. [11]; the actually used values are collected in Table 1. I_{SiC} -s values for Si_{LVV} and Si_{KLL} Auger electrons

Si	С	SiC

Si _{LVV} ; 92 eV	0.39	0.46	0.39
Si _{KLL} ; 1620 eV	3.3	3.8	3.1
Table 1. The electron effective- attenuation-lengths in units of nm for signal electrons			
with energies of 92 eV and 1620 eV in pure Si, C, SiC. Data were calculated based on the			
software given by Powell et. al [9].	-		

are measured at the end of the depth profiling (when all layers are removed). The initial thicknesses and X_b are fitting parameters for simulation of the measured depth profile.

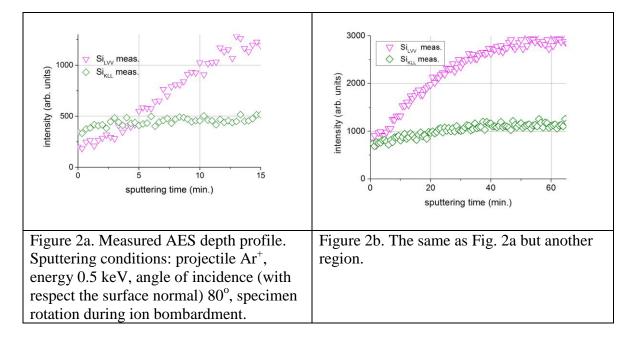
2.1.2 Calculation of sputter removal.

Applying j_{ion} ion current density for Δt time for sputter removal, the removed layer thickness Δd is $\Delta d = N^{1/3} j_{ion} \Delta t Y$, where, N is the atomic density of the removed material, while Y is the total sputtering yield.

To avoid large scale ion bombardment induced damage we applied low energy (0.5 keV) and grazing angle of incidence (80° with respect to the surface normal) Ar⁺ ion bombardment for depth profiling and sample was rotated during sputtering. The sputtering yield values at these parameters are rarely available, however. Thus, the relative sputtering yield has been measured for these parameters by sputtering away a thin bilayer of C/Si of known thickness; both elements were in amorphous form. The relative sputtering yield, Y_C/Y_{Si} , (0.5 keV, 80°) was found to be ~ 2. In the multi-components part of the sample (in the buffer layer) it was assumed that the sputtering yield can be given as $Y=\Sigma X_i Y_i$.

3. Experimental results

Fig. 2a and b show two typical depth profiles (the change of the corresponding Auger electron intensities as a function of the sputtering time). In the simplest case



(homogeneous overlayer not containing elements of the substrate) exponential increase of

the signal electrons intensities is expected; as opposed to that seen in Fig. 2a and b. Still, a rough estimate of the thickness can be taken assuming this simplest case. In the case of depth profile shown in Fig. 2a, the thicknesses based on the intensity change during the depth profiling process for the Si_{LVV} (EAL=0.4 nm) and Si_{KLL} (EAL=3 nm) Auger electrons intensities are, 0.9 nm and 0.7 nm. We might hope that performing a more rigorous evaluation, the thickness of the homogeneous overlayer can be determined. Calculating the same values for the depth profile shown in Fig. 2b we get 1.2 nm (based on Si_{KLL} Auger electron intensities), while 0.5 nm if we consider the intensity change of the Si_{LVV} Auger electron intensity. This big difference cannot be handled considering a single homogeneous overlayer; it will be shown that the area irradiated by the exciting electron beam contains regions of various thicknesses.

4. Discussion and simulation of the depth profiles

The attenuation of the signal electrons depends exponentially on the thickness of layer that they travel through. Thus, if the thickness of the layer of interest is similar to that of the attenuation length of the measured electron, the thickness can be determined rather accurately. In the present case the EAL-s for Si_{LVV} and Si_{KLL} Auger electrons in C matrix are 0.4 nm and 3.6 nm, respectively [11]. This is why AES was proposed as a possible method for determining the thickness of the graphene layer, since by simply measuring the intensity of the substrate Auger line the thickness in a relatively wide range can be determined.

If we apply depth profiling the accumulated data allows for a more accurate thickness determination. The objection against depth profiling using ion removal might be that it is a destructive method, which alters the material and thus, impairs the information. Therefore we will first discuss the possible harms of the ion bombardment and later we will determine what the accuracy of the method is.

It is well known that ion bombardment might cause serious alteration of the bombarded material including morphology change, ion bombardment induced mixing, bombardment induced segregation, various radiation damages, etc. For the case of graphene various ion bombarded induced damages have been reported. Lucchese et al. subjected a single layer graphene (made by peeling layers from highly oriented pyrolytic graphite) to Ar⁺ ion bombardment of energy 0.09 keV and measured the damage by means of Raman spectroscopy [14]. It was concluded that even this very low energy ion impact causes disorder, that is, the original atomic arrangement was altered [14]. Al-Harthi et al. [15]

studied the effect of ion bombardment on few layer graphene (made by peeling layers from highly oriented pyrolytic graphite) applying a wide range of ion energy at angle of incidence of 45° without applying specimen rotation. They detected ripple formation, and damage (transformation of sp_2 bonds to sp_3 ones) even at ion energy of 0.5 keV. Siokoua et al. produced a graphene layer on Cu surface and applied 0.4 keV Ar⁺ bombardment observing the disappearance of a characteristic loss peak of graphene [16], showing the damage of the sp_2 network.

Based on these observations we should conclude that the sp_2 network is rather sensitive to ion bombardment even using extreme low energies and might be destroyed during our sputter removal procedure. It should be added that this type of damage does not affect our thickness measurement; the attenuation of the electrons most likely changes only slightly with the appearance of the defects. The ripple formation reported by Al-Harthi et al. [15] and the possible ion bombardment induced mixing should be considered seriously, however.

Considering the ripple formation, that is, ion bombardment induced morphology development we should emphasize that in the quoted study [15] the angle of incidence was 45° and no specimen rotation was used. Both conditions are rather disadvantageous from the point of view of ion bombardment induced morphology development. It has been known for a long time that the ion bombardment induced morphology development can be considerably reduced by using Zalar (sample) rotation [17] during ion bombardment. Kovac et al. [18] also reported ripple formation on bulk (50 nm thick) C sample at 1 keV Ar⁺ ion bombardment for various parameters, but they also showed the disappearance of ripples if specimen rotation had been used. It is also well established

that the usage of grazing angle of incidence for ion bombardment also reduces the morphology development [19]. Moreover, it should also be mentioned that the ion bombardment induced morphology change is proportional to the removed layer thickness [19,20]. Since the layer thickness to be removed in the present case is in the range of 1-2 nm, and we apply specimen rotation during sputtering and grazing angle of incidence we do not expect such morphology development which could impair measurement of the layer thickness.

To deal with ion bombardment induced mixing it is to be recalled that the sputtering yield of carbon strongly changes with the angle of incidence and is high at grazing angle of incidence [21]. This behavior was explained based on *The Stopping and Range of Ions in Matter* (SRIM) [22] model applying a binary interaction approximation. This model predicts a weak interaction between the bombarding Ar^+ ions and carbon based matrix. Thus, the penetration length (projected range) of the Ar^+ ions at grazing angle of incidence is low (resulting in an increase of the sputtering yield) causing a moderate ion induced mixing, which will be ignored.

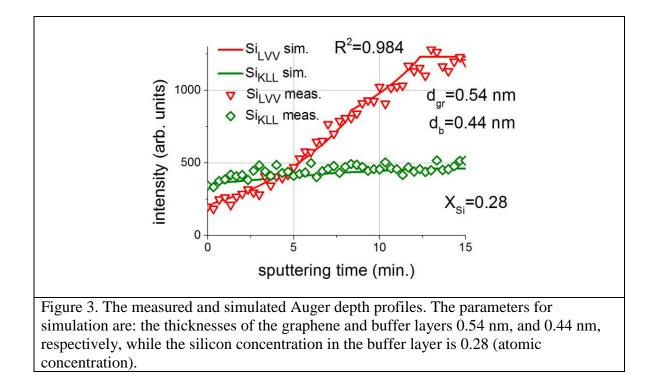
Summarizing: a. / ion bombardment might destroy the sp_2 network thus, we will not attempt to distinguish between contamination carbon and graphene, b./ the thickness measurement is most likely not affected by ion bombardment.

Based on the above, the overlayer will be assumed as follows: a graphene layer (graphene and if present C contamination) and a buffer layer.

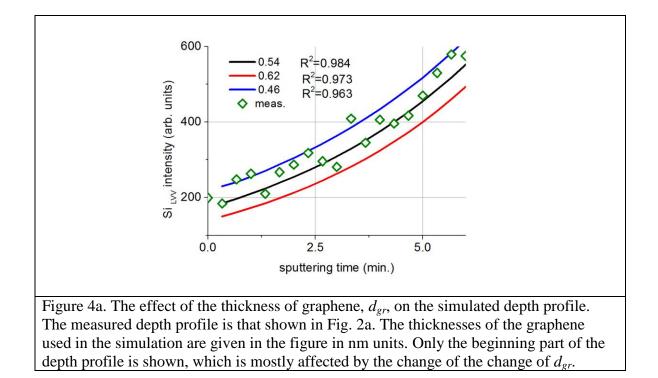
4.1 Simulation of the depth profile shown in Fig. 2a.

During the depth profiling process first the graphene layer and then the buffer layer is removed and the final condition is a pure SiC surface providing the intensities of the Auger electrons of the substrate without attenuation. The intensities of the Auger electrons as a function of depth is calculated based on equations 1 and 2, where the thickness d_c is taken to be 0; the contamination C will not be distinguished from the graphene. The density of the buffer layer is equal to that of graphene [13]. The EAL-s were calculated by the software of ref. 11 and the applied values are collected in Table 1. The change of the intensity Si_{KLL} Auger electrons is small during the depth profiling and thus the desired parameters cannot be derived with reasonable accuracy. Therefore those results will not be discussed.

The shape of the depth profile depends on all parameters used in the simulation. Still because of the low EAL-s the effect of the various parameters can be studied independently considering the corresponding part of the depth profile. For the simulation of the depth profiles shown in Fig. 2a the Si concentration X_b and the thickness d_b of the buffer layer, and the thickness of the graphene layer d_{gr} will be used as fitting parameters and the simple R^2 method $(R^2 = 1 - \Sigma(y_i - f_i)^2 / \Sigma(y_i - \tilde{y}_i)^2)$ where y_i, \tilde{y}_i and f_i are the measured, average and fitting values, respectively) will be applied to characterize the quality of the fitting. Fig. 3 shows the simulated and measured curves, using the following fitting parameters: $d_{gr} = 0.54$ nm, $d_b = 0.44$ nm $X_b = 0.28$. The R^2 value is 0.984, which means that the fitting is reasonably good.

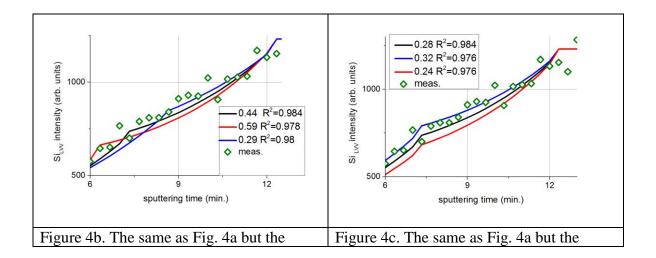


It is important to determine the range of the acceptable parameters, that is, the error of the fitting parameters. To do this we simply varied one of the parameters (keeping the others constant) until the deviation of the simulated depth profile from the measured one was well visible. E. g. the graphene layer thickness could be varied by \pm 15 % (0.62 nm and 0.44 nm) to reach a well visible difference, which is also shown by the corresponding R^2 values. They were found to be 0.973 and 0.963 for d_{gr} values of 0.62 nm and 0.44 nm, respectively. The results are shown in Fig. 4a. Fig. 4a shows only the "graphene part" of the depth profile, which is the most affected by changing the graphene thickness.



Thus we conclude that the accuracy of the d_{gr} value is about 15%.

The same type of calculations can be performed with varying the thickness and concentration values of the buffer layer; the results are shown in Fig. 4b and 4c. Again the figures show only that part of the depth profiles which were mostly affected by the variation of the given parameter.



buffer layer thickness is varied; the	buffer layer concentration is varied; the
thickness values are shown in the figure in	concentration values are shown in the
nm units.	figure in atomic concentration units.

In the case of the determination of buffer layer thickness our accuracy is poor as it can be seen in Fig. 4b; 35% change of the buffer layer thickness (d_b increases and decreases from the optimum 0.44 nm to 0.59 nm and 0.29 nm, respectively) results in a hardly visible change (R^2 decreases from 0.984 to 0.978) of the fitted curve. This behavior can easily be understood. If buffer layer thickness is increased then the Si Auger signal originating from the SiC exponentially decreases but the Si signal emitted from the buffer layer increases partly compensating the decrease. Similarly if the thickness of the buffer layer is decreased then the Si signal originating from SiC increases, while the Si signal emitted by the buffer layer decreases.

On the contrary the fitting is sensitive to the Si concentration of the buffer layer X_b ; about ± 15 % change (0.28 ± 0.04) of X_b results a well visible deviation (R^2 decreases from 0.984 to 0.976).

4.2. Simulation of the depth profile shown in Fig. 2 b

The rough estimation showed that the simulation of this depth profile is more difficult than that shown in Fig. 2a. The problem is that the ratio of the Si_{KLL} and Si_{LVV} Auger electron intensities, measured at the beginning of the depth profiling, cannot be simulated by considering a layer system with a homogeneous layer thickness used above. This ratio can only be simulated if we suppose a layer structure of varying layer thickness. Actually if we suppose that part of the analyzed area is covered by a thin layer, while the reminding part of the sample with a much thicker one we can consolidate the measured ratios; the relatively low intensity of the Si_{KLL} Auger electrons is explained by the thick

layer, while the relatively high intensity of the Si_{LVV} Auger electrons is explained by the analyzed region covered by the thin layer.

To perform the simulation for a region exhibiting such inhomogeneity we will assume the presence of two or more homogeneous region of various thicknesses within the analyzed area. Thus, besides the parameters, d_{gr} , d_b , X_b , used before, a new parameter should be introduced the coverage, Θ , of the homogeneous region (determined by a single set of d_{gr} , d_b , X_b ,). In this case there is a considerably change of the Si_{KLL} profile, thus this data set can be fitted with reasonable accuracy improving the accuracy of the simulation. Fig. 5 shows the result of such a fitting. The depth profiles shown in Fig. 5 were recorded from an area with a diameter of 50 µm.

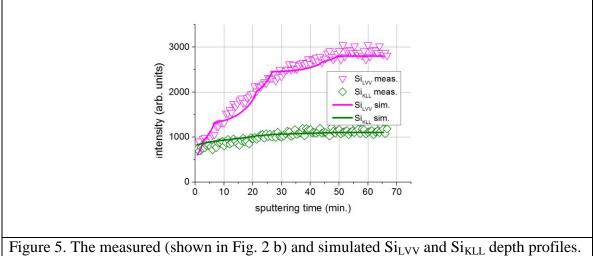


Figure 5. The measured (shown in Fig. 2 b) and simulated Si_{LVV} and Si_{KLL} depth profiles. In this case inhomogeneous surface coverage was assumed; the parameters for simulation are given in Table 2.

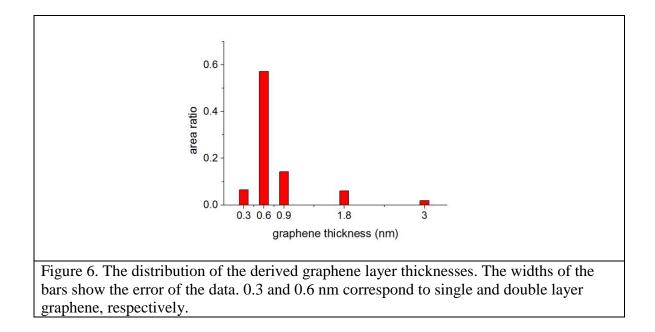
Coverage	d_{gr}	d_b	X_b
(Θ)	a_{gr} (nm)	(<i>nm</i>)	(at %)
0.45	0.3	0.4	0.3
0.42	1.8	0.4	0.3

0.13	3.0	0.4	0.3
Table 2. The graphene, d_{gr} , buffer, d_b , layer thicknesses and the Si concentration, X_b , in			
the buffer layer and the coverage of the three homogeneous regions derived from the			
measured depth profile shown in Fig. 2 b. The thicknesses are given in nm, the			
concentration in atomic concentration. The fitted curve is shown in Fig. 5.			

Table 2 shows that somewhat less than half the analyzed region is covered by a single graphene layer. About 40% of the analyzed region is covered by a thick layer which most likely is made of ML graphene and C contamination. The reminder 10% of the analyzed region is covered by a thick layer most likely contamination.

4.3. Determination of the thickness distribution of the graphene layer.

For the determination of the thickness distribution of a graphene layer produced by some technology the following procedure is followed. First AES spectra are recorded on various places. Considering the Si_{LVV}/Si_{KLL} ratios one can choose the typical and /or strange regions using proper weights where it is advisable to record AES depth profiles. The number of points chosen should represent the average occurrence of the various types of Si_{LVV}/Si_{KLL} ratios. Having a scanning ion beam the whole area of interest can be sputtered simultaneously and applying multi-point AES analysis depth profiles in all areas chosen can be recorded. All depth profiles provide one or more (with area ratios) d_{gr} , d_b and X_b values. Since all depth profiles were recoded from the same area ($25^2 \pi$ µm²) we can easily get the thickness distribution of the surface studied by simply adding the thickness values. Such a thickness distribution is shown in Fig. 6.



It is clear that the majority of the surface, about 60%, of our specimen is covered by a graphene layer with a thickness of 0.6 ± 0.15 nm, which corresponds to 2 ML graphene. 14% of the surface is covered by a layer of a thickness of 0.9 nm, which might be 3 ML graphene. Only 6% of the surface is covered by 0.3 nm thick layer, single layer graphene and a similar area is covered by a thick layer, 1.8 nm, ML graphene and probably contamination. Only about 2 % of the studied area is covered by a 3 nm thick layer which might contain C contamination as well. Such contaminations are adsorbates on graphene surface that appear due to long-term exposure to atmospheric conditions. The calculation automatically provides similar distributions of the buffer layer thickness and Si concentration in the buffer layer. It turns out that the buffer layer thickness, d_b , and the Si concentration of the buffer layer, X_b , are rather homogeneous. The thickness of the buffer layer is 0.4 nm on the 85% of the studied area, while 15% of the surface contains buffer layer with thickness of 0.2 nm. The Si concentration of the buffer layer is around 0.3 atomic concentration.

These results verify that AES depth profiling can be meaningfully used for the determination of the thickness distribution of a graphene sheet of macroscopic size.

5. Conclusions

AES depth profiling using gentle ion sputtering conditions (ion energy 0.5 keV, angle of incidence 80, rotated specimen) was carried out on several areas (diameter 50 µm) of a graphene layer grown on SiC surface. Due to the possible beam damage the graphene and graphite contamination could not be separated based on the Auger lines, thus these two components were not distinguished. The measurement clearly showed the presence of the buffer layer. It was possible to derive the thicknesses of the graphene and buffer layer and the Si concentration of the buffer layer by fitting the measured depth profile by the simulated one. The latter result confirms the presence of unsaturated Si bonds in the buffer layer thus evidencing the accuracy of the applied AES profiling method. Depth profiles recorded from several points of the sample resulted in a thickness distribution of the layer. This way we have shown that the method can be applied for the determination of the thickness distribution of a graphene sheet of macroscopic size.

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References

- M. Xu, D. Fujita, J. Gao, N. Hanagata, Auger Electron Spectroscopy: A Rational Method for Determining Thickness of Graphene Films, ACS Nano 4 (2010) 2937-2945.
- V. Darakchieva, A. Boosalis, A.A. Zakharov, T. Hofmann, M. Schubert, T.E. Tiwald, T. Iakimov, R. Vasiliauskas, R. Yakimova, Large-area microfocal spectroscopic ellipsometry mapping of thickness and electronic properties of epitaxial graphene on Si- and C-face of 3C-SiC(111), Appl. Phys. Let. 102 (2013) 213116.
- A. Ruammaitree, H. Nakahara, K. Akimoto, K. Soda, Y. Saito, Determination of nonuniform graphene thickness on SiC (0 0 0 1) by X-ray diffraction, Appl. Sur. Sci. 282 (2013) 297–301.
- C. Berger, Z. Song, T. Li, X. Li, A.Y. Ogbazghi, R. Feng, Z. Dai, A.N. Marchenkov, E.H. Conrad, P.N. First, W.A. de Heer, Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene-based Nanoelectronics, J. Phys. Chem. B 108 (2004) 19912-19916.
- E. Rollings, G.H. Gweon, S.Y. Zhou, B.S. Mun, J.L. McChesney, B.S. Hussain, A.V. Fedorov, P.N. First, W.A. de Heer, A. Lanzara, Synthesis and characterization of atomically thin graphite films on a silicon carbide substrate, J. Phys. Chem. Solids 67 (2006) 2172–2177.
- S. Tanuma, C.J. Powell, D.R. Penn, Calculation of electron inelastic mean free paths, Surf. Interf. Anal. 17 (1991) 911–926.

- C. Virojanadara, M. Syväjarvi, R. Yakimova, L.I. Johansson, A.A. Zakharov, T. Balasubramanian, Homogeneous large-area graphene layer growth on 6H-SiC(0001), Phy. Rev. B 78 (2008) 245403.
- A. Barna, M. Menyhard, Auger depth profile analysis of deeply buried interfaces, Phys. Stat Sol. (a) 145 (1994) 263-274.
- M. Menyhard, High-depth-resolution Auger depth profiling/atomic mixing, Micron 30 (1999) 255–265.
- L. Zommer, A. Jablonski, L. Kotis, G. Safran, M. Menyhard, Simulation and measurement of AES depth profiles; a case study of the C/Ta/C/Si system, Surf. Sci. 604 (2010) 633–640.
- NIST Standard Reference Database 82; NIST Effective-attenuation-length Database (C.J. Powell, A. Jablonski Gaithersburg 2001).
- 12. T. Filleter, K.V. Emtsev, Th. Seyller, R. Bennewitz, Local work function measurements of epitaxial graphene, Appl. Phys. Lett. 93 (2008) 133177.
- S. Golera, C. Colettia, V. Piazza, P. Pingue, F. Colangelo, V. Pellegrini, K.V. Emtsev, S. Forti, U. Starke, F. Beltram, S. Heun, Revealing the atomic structure of the buffer layer between SiC(0001) and epitaxial graphene, Carbon 51 (2013) 249– 254.
- M.M. Lucchese, F. Stavale, F. Martins, E.H. Ferreira, C. Vilani, V.O.H. Moutinho, R.B. Capaz, C.A. Achete, A. Jorio, Quantifying ion-induced defects and Raman relaxation length in graphene, Carbon 48 (2010) 1592 –1597.
- 15. S.H. Al-Harthi, M. Elzain, M. Al-Barwani, A. Kora, T. Hysen, M.T.Z. Myint, M.R. Anantharaman, Unusual surface and edge morphologies, sp2 to sp3 hybridized

transformation and electronic damage after Ar^+ ion irradiation of few-layer graphene surfaces, Nanoscale Research Letters 7 (2012) 466.

- 16. A. Siokoua, F. Ravani, S. Karakalos, O. Frank, M. Kalbacc, C. Galiotis, Surface refinement and electronic properties of graphene layers grown on copper substrate: An XPS, UPS and EELS study, Appl. Surf. Sci. 275 (2011) 9785–9790.
- A. Zalar, Improved depth resolution by sample rotation during Auger Electron Spectroscopy depth profiling, Thin Solid Films 124 (1985) 223–230.
- J. Kovač, A. Zalar, B. Praček, Ripple structures developed on graphite layers during ion-sputtering, Surf. Interface Anal. 38 (2006) 300–304.
- A. Barna, Topographic kinetics and practice of low angle ion beam thinning. In Proc.
 Fall Meeting MRS, Boston, Workshop on Specimen Preparation for Transmission
 Electron Microscopy of Materials-III, MRS Conf. Ser. 254 (1992) 3–22.
- M.A. Makeev, A.L. Barabasi, Ion-induced effective surface diffusion in ion sputtering, Appl. Phys. Lett. 71 (1997) 2800–2802.
- A. Barna, M. Menyhard, L. Kotis, G.J. Kovacs, G. Radnoczi, A. Zalar, P. Panjan, Unexpectedly high sputtering yield of carbon at grazing angle of incidence ion bombardment, J. Appl. Phys. 98 (2005) 24901-6.
- 22. J.F. Ziegler, Stopping and Range of Ions in Matter, freely available from <u>www.srim.org</u>.