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UTILIZING OF THE MEDIUM-ENERGY ION SCATTERING SPECTROMETRY FOR THE COMPOSITION INVESTIGATION OF GRAPHENE OXIDE FILMS ON SILICON SURFACE

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The possibilities of Medium-Energy Ion Scattering (MEIS) spectrometry combined with ion channeling for the estimation of the composition of single layer graphene oxide films and produced graphene layers deposited on the surface of standard silicon substrates was investigated. It was found that the oxygen amount in the natural surface silicon oxide ranges from 2-8 times the possible oxygen content in a graphene oxide layer. This causes difficulties in the estimation of the oxygen concentration in graphene oxide deposited on such substrates. The proposed method of preliminary single hydrogen cathode surface processing in electroplating bath leads to the significant decrease of surface layer oxygen content which results in an increase in the accuracy of reduced graphene oxide composition estimation.

Keywords: graphene oxide, silicon oxide, Rutherford Backscattering Spectrometry.

The main obstacle in the creation of graphene-based field-effect transistors is the band gap absence in this material [1]. The latest studies showed the possibility of controlled bandgap width graphene layers production by means of thermal reduction of graphene oxide films on Si surface [2]. In this process, the evaluation of the graphene film composition, as well as the estimation of the bandgap width dependence and carrier mobility, on the remaining oxygen concentration becomes the experimental task of particular importance.

We investigated the possibilities of Medium-Energy Ion Scattering (MEIS) spectrometry combined with ion channeling in order to estimate the composition of near-surface layers of crystalline silicon as well as of graphene oxide films deposited on the surface of silicon substrates. MEIS, being a modification of Rutherford Back Scattering (RBS) spectrometry, differs from the latter by the possibility of achieving extremely high depth resolution in the elemental analysis of near-surface layers due to the utilization of high energy resolution electrostatic analyzers. For current work conditions (scattering of H^+ ions having the initial energy of 96 keV in silicon) the depth resolution was on the order of 1 nm. Using an aligned (channeling) spectra measurement regime, in which the probe ion beam direction was coincident with the low-index crystalline axis one (in our case it was <100> direction) made it possible to decrease dozens of times, relative to “random” regime, the signal of ions, back scattered from the bulk of single crystal silicon substrate, keeping the signal from amorphous layers. That resulted in a significant increase in the accuracy for the estimation of carbon and oxygen atom content and their depth distribution.

Oxygen content measurements were carried out for for the natural oxide substrates, whereas for ”substrate plus graphene oxide” structures, measurements were made to determine the carbon and oxygen contents and their depth distributions.

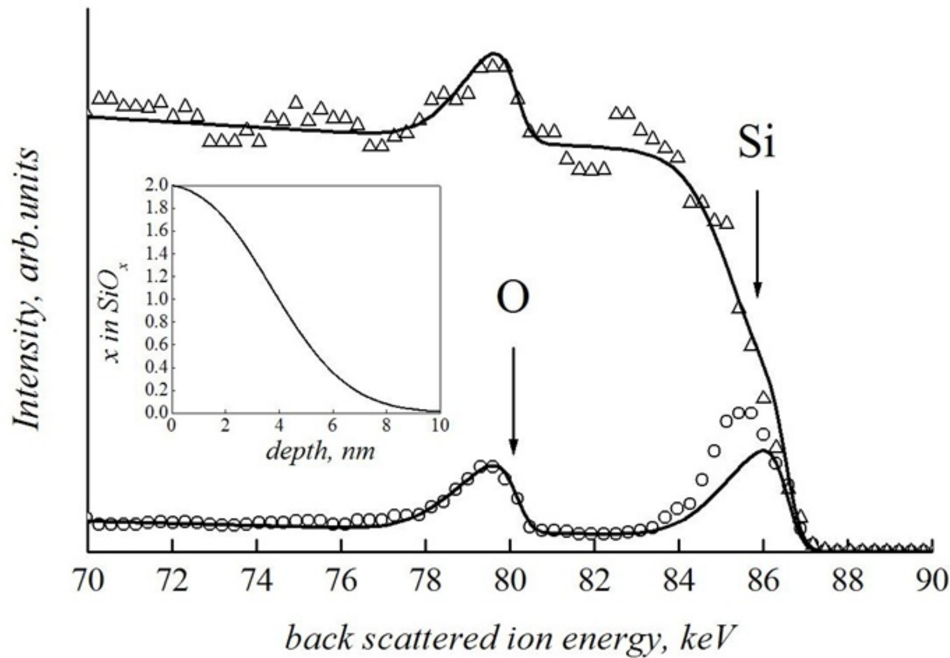

FIG. 1. The energy spectra of H^+ ions having the initial energy of 96 keV back scattered from pure silicon with natural surface oxide. Circles — aligned regime, triangles — "random" regime, solid curves — the result of computer simulation. Insert — the depth distribution of oxygen

Fig. 1 shows the energy spectra of H^+ ions, back scattered from the sample of a single silicon crystal with natural oxide. Arrows point to the energies of ions, back scattered from silicon (86 keV) and oxygen (80 keV) atoms of the sample surface. Solid lines are the result of computer simulation for "random" and aligned measurement regimes. Hereafter (e.g. Fig. 3), the aligned spectra simulation of near-surface layers took into account only the signal from silicon of the oxide layer, ignoring that of so called "surface peak" of ion scattering on pure silicon, and that is the reason for the discrepancy in the 84-86 keV region. Comparison of the spectra shows that the accuracy of the signal detection, corresponding to ion back scattering on oxygen in the aligned regime is significantly higher because the background bulk silicon signal is approximately suppressed nearly 20-fold. The computer simulation made it possible to determine the whole oxygen amount in natural oxide; in this particular case it was 16×10^{15} atoms/cm^2.

The "protacted" back (low energy) oxygen peak front (energies 77-80 keV) indicates a gradual oxygen concentration decrease from the surface to deeper layers. The depth dependence of oxygen concentration is shown in the insert in Fig 1. It is interesting to note, that the same phenomenon was observed in [3], devoted to MEIS investigation of artificially created oxide layers on silicon surface.

The oxygen content in the investigated substrates was found to range from 6×10^{15} to 19×10^{15} atoms/cm^2. For comparison, it should be noted that if the carbon atom content in the graphene oxide layer is 3.8×10^{15} atoms/cm^2 and each carbon atom accounts for a single oxygen atom (it corresponds to maximal oxidation rate), the tight to carbon oxygen monolayer must also contain 3.8×10^{15} atoms/cm^2. This means that the oxygen of the natural oxide significantly affects the accuracy when estimating the oxidation rate. In order to reduce the oxygen content, the single hydrogen cathode surface processing in electroplating bath

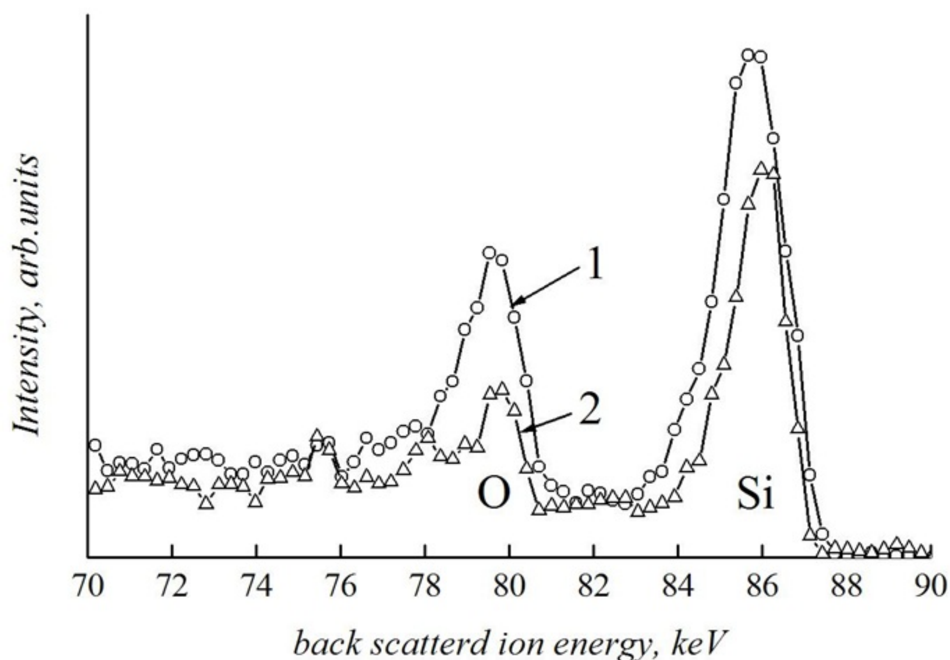

FIG. 2. The energy spectra of H^+ ions having the initial energy of 96 keV back scattered from silicon substrate before (1) and after (2) the processing in electroplating bath

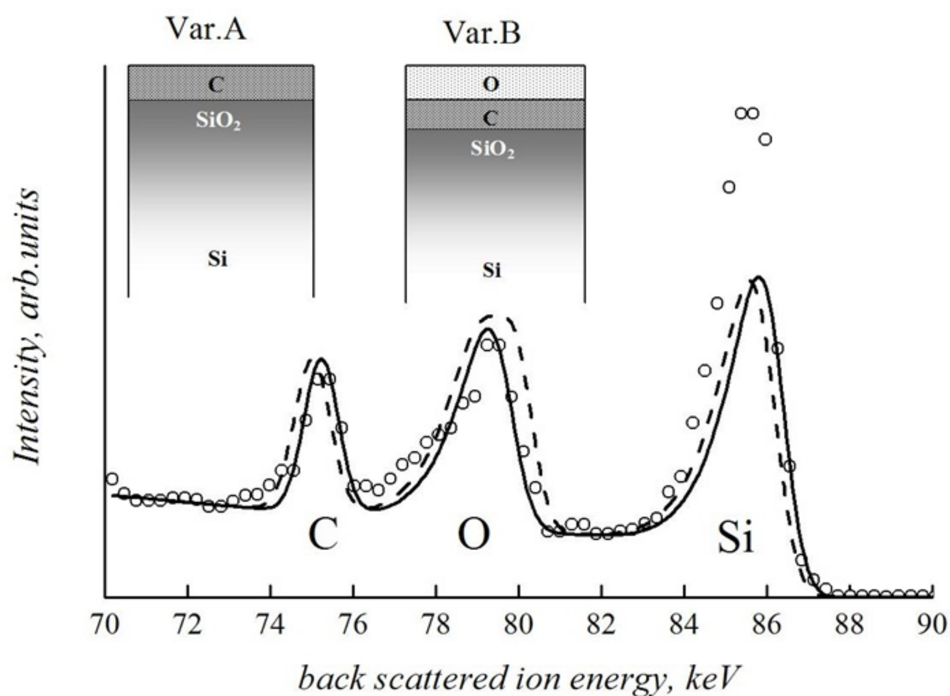

FIG. 3. The energy spectra of H^+ ions having the initial energy of 96 keV back scattered from graphene oxide layer, deposited on the silicon substrate. Circles — experiment, solid line — the MEIS computer simulation for the structure, schematically depicted in the insert Var.A, dashed line – the same for the structure depicted in Var.B insert

was applied. In Fig. 2 the MEIS substrate spectra before (1) and after (2) this processing are shown. The oxygen contents were found to be 16×10^{15} atoms/cm^2 and 8×10^{15} atoms/cm^2, respectively, i.e. the processing used halved the amount of oxygen in the surface oxide layer.

The MEIS aligned spectrum of sample having the structure "silicon substrate with the natural oxide plus graphene oxide layer" is shown in Fig. 3. Circles depict experimental results, while lines show the computer simulation for two modeling structures: solid — for one schematically depicted in Var.A insert and consisting of silicon, its oxide and graphene. With the help of computer simulation, the carbon and oxygen contents were found to be 7×10^{15} atoms/cm^2 and 10×10^{15} atoms/cm^2, respectively. It is important to note, that all three fore fronts (high energy) of silicon, oxygen and carbon calculated peaks coincided with experimental ones. Dashed curve shows the result of modeling of the structure, depicted in Var.B insert, where the oxygen monolayer of $\sim4\times10^{15}$ atoms/cm^2 laying above the graphene film was added. In this variant, the essential discrepancy was observed for all fore fronts, leading one to conclude that there is no covering oxygen layer, at least of the amount, similar to that of the complete monolayer. Comparison of the simulated and experimental spectra demonstrated the high MEIS sensitivity to graphene's oxidation rate.

Accordingly, the described investigations allow one to draw the conclusion that MEIS-based diagnostics, when applied to the solving of silicon-graphene structures synthetic problems, is rather promising and can give much pertinent information.

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