

A compact high-resolution elastic recoil detection system for lithium depth profiling

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A compact high-resolution elastic recoil detection analysis (ERDA) system was developed for precise Li analysis. 200 - 400 keV He⁺ ions were used as primary ions and the energy spectra of recoiled Li ions were measured using a magnetic spectrometer. Due to its dispersion the background originating from the scattered primary ions is reduced. The recoiled ions of the substrate other than Li, which may also contribute to the background, were rejected by a thin mylar foil placed in front of a focal plane detector. An electrostatic quadrupole lens was installed at the entrance of the magnetic spectrometer to improve the depth resolution by correcting the effect of the kinematic broadening. The performance of the developed high-resolution ERDA was examined by measuring several samples. A thin Li layer ($1.5 \times 10^{15} \text{ cm}^{-2}$) deposited on a graphite surface was clearly observed and the detection limit was estimated to be less than 0.01 ML under typical measurement conditions. The depth resolution was estimated to be 0.5 nm at the surface and was better than 3 nm in the surface region within 5 nm from the surface.

1. Introduction

Lithium ion batteries are widely used as power sources for portable electronics, electric vehicles *etc.* Because intercalation of lithium into the electrodes is one of the key processes in the Li ion batteries, understanding of the intercalation mechanism is of prime importance to improve battery performance [1]. To this end, precise analysis of Li at the electrode surfaces is required. Elastic recoil detection analysis (ERDA) is one of the powerful techniques for depth profiling of light elements. Dollinger *et al* developed a high-resolution ERDA with a sub-nm depth resolution using a sophisticated magnetic spectrograph [2, 3]. This allows depth profiling of light elements with a depth resolution of ~ 0.5 nm at the surface and with a sensitivity down to the 100 ppm level. They used a rather large magnetic spectrograph originally designed for nuclear physics experiments [4] and a large tandem accelerator (14 MV tandem accelerator) to utilize high energy heavy ions, *e.g.* 100 MeV Au ions. Although the performance of their high-resolution ERDA is excellent, need of such a big facility prevents it from spreading into wide application fields. There was another approach to develop high-resolution ERDA using a relatively small accelerator (*e.g.* 2MV tandem accelerator) [5]. Vandervorst and his coworkers employed a time of flight (TOF) detection system in combination with relatively low energy (< 20 MeV) heavy ions (Cl ion, Cu ion *etc.*). The achieved depth resolution, however, is several nm, which may not be good enough for some applications. We have developed a compact high-resolution ERDA system for precise Li analysis with a sub-nm depth resolution using a small magnetic spectrometer and a small accelerator. The aim of the present paper is to describe the performance of the developed system.

2. Rejection of scattered primary ions

In ERDA, primary ions scattered from the specimen contribute to a background in the energy spectrum. In the conventional ERDA for hydrogen analysis, the scattered primary ions are rejected by a thin foil installed in front of a silicon surface barrier detector [6]. The foil, however, deteriorates the depth resolution due to the energy loss straggling of the recoiled ions during the passage through the foil. In the high-resolution ERDA, a

position-sensitive ionization chamber which can measure the position and ion species simultaneously is used as a focal plane detector of the magnetic spectrograph. Using such a detector, the energy spectrum of recoiled ions of a specific element can be measured separately from other ions [3]. In the present ERDA system, however, such a focal plane detector cannot be used because the energies of the recoiled ions are only several hundred keV and far below the detection limit of such a detector. In order to reject the scattered primary ions, we employ He ion beam as a probe instead of heavy ions. When the magnetic field of the spectrometer is adjusted for the recoiled Li ions, scattered He ions are deflected at larger angles and cannot reach the focal plane detector. For example, when a 400 keV He beam is used as a primary beam the energy of Li ions recoiled at 25° with respect to the incident beam is about 304 keV. If the magnetic field is adjusted to pass 304 keV Li^+ ions, both 532 keV He^+ and 2128 keV He^{2+} ions can pass through the magnetic spectrometer. However, the actual energies of the scattered He ions are, of course, lower than the primary energy, 400 keV. Thus there is no background originating from the scattered primary ions in the ERDA spectrum.

3. Experimental

A schematic drawing of our high-resolution ERDA setup is shown in Fig. 1. Beams of 200 – 400 keV He^+ ions were produced by a small accelerator and collimated by a couple of slit systems to $2 \times 2 \text{ mm}^2$ in size. The beam current was monitored by a beam chopper installed just before the scattering chamber and a typical beam current was $\sim 50 \text{ nA}$. The collimated He^+ beam was sent to a scattering chamber (base pressure $2 \times 10^{-8} \text{ Pa}$), where a sample was mounted on a 5-axis precision goniometer. The ions recoiled by the He^+ ions at 25° with an exit angle of 10° with respect to the surface plane were analyzed by a 90° sector magnetic spectrometer and detected by a one-dimensional position-sensitive detector (1D-PSD) consisting of Z-stack micro channel plates (MCPs) and a resistive anode (effective length 100 mm). The energy dispersion ($E dx/dE$, where x is the position on the focal plane) of the spectrometer is 400 mm and the acceptance angle of the spectrometer is $\pm 10 \text{ mrad}$ both in the vertical and horizontal directions. Although the acceptance angle is not

so large, a so-called kinematic broadening causes deterioration in the depth resolution. In the present case, the kinematic broadening is calculated to be 1.9% of the recoiled energy, which corresponds to a depth resolution of a few nm under typical experimental conditions. In order to correct the effect of the kinematical broadening, an electrostatic quadrupole lens (Q-lens) was installed between the sample and the spectrometer. Using the Q-lens, the Li^+ ions recoiled from surface atoms at different angles within the acceptance angle can be focused on the same position in the energy dispersive plane of the detector.

4. Result and discussion

A highly oriented polycrystalline graphite (HOPG) was mounted on the goniometer. A small amount of Li was deposited *in situ* on the surface. The amount of Li was measured to be $1.5 \times 10^{15} \text{ cm}^{-2}$ (corresponding to 0.4 ML of graphite) using high-resolution Rutherford backscattering spectroscopy (RBS) after ERDA measurements. In the high-resolution RBS measurement, a different area was used to avoid a possible modification due to ERDA measurements. Figure 2 shows an example of the observed ERDA spectra for the Li-deposited graphite sample (solid circles) using a 200 keV He^+ beam. There is a small peak at $\sim 152 \text{ keV}$, which corresponds to the deposited surface Li. Although there should be no background originating from the scattered He ions as was mentioned above, there is in fact a large background. The origin of the observed background may be ascribed to the recoiled carbon ions. The recoiled 88 keV C^+ ions have the same trajectory as the 152 keV Li^+ ion in the magnetic spectrometers and these ions contribute to the observed background. In order to reject this large background, a mylar foil (thickness $0.5 \mu\text{m}$) was installed in front of the 1D-PSD (9mm from the MCP entrance surface). A thin Al layer (20 nm) was deposited on the mylar surface to prevent possible charging. The thickness of the foil was chosen so that the projected range of 88 keV C^+ (152 keV Li^+) is shorter (longer) than the foil thickness. The passage of the Li ions through the foil hardly deteriorates the energy resolution of the spectrometer because the energy analysis of the recoiled Li ions has already been completed when the ion pass through the foil. The only possible deterioration comes from the angular spread due to multiple scattering in the foil. The angular distribution of Li ions passing

through the mylar foil was calculated using the TRIM code [7]. The calculated FWHM is 0.3 and 0.13 rad for 152 and 304 keV Li ions, respectively. These angular spread result in the spatial spread of 2.7 and 1.2 mm, respectively, on the MCP surface, which corresponds to the energy resolution of 1.0 and 0.9 keV, respectively.

The observed ERDA spectrum with the mylar foil is shown by open circles in Fig. 2. The background was reduced by a factor of 100 and the Li peak is clearly seen. Note that there is a long tail in the low energy side of the Li peak, which cannot be seen without the foil. This tail indicates that a part of deposited Li atoms penetrate through the surface and distribute in the sub-surface region of a few nm from the surface. There is still a residual background, which is ascribed to the dark noise of the MCP (~ 0.07 counts $\text{cm}^{-2} \text{s}^{-1}$ in the present case). By integrating the spectrum in the energy region from 145 to 154.5 keV, the total yield of the Li peak was calculated to be ~ 1100 counts. The background yield in the corresponding region is ~ 180 counts. Thus the net counts of the Li signal is 900 ± 36 ($= \sqrt{1100 + 180}$) in the present case (1.5×10^{15} Li atoms cm^{-2}). If the detection limit is defined so that the net counts is equal to the statistical error, the detection limit of surface Li on a graphite surface is estimated to be $3 \times 10^{13} \text{ cm}^{-2}$, which corresponds to ~ 0.008 ML, under the present experimental conditions ($50 \text{ nA} \times 1000 \text{ s}$). Note that the detection limit could be improved by increasing the measurement time because the net counts increases linearly with measurement time while the statistical error increases more slowly.

Figure 3 shows another examples of the observed ERDA spectrum using 400 keV He^+ ions. The sample was prepared by vacuum evaporation of LiF on Si(001). The thickness of the LiF layer was measured to be 3 nm using high-resolution RBS. The open circles show the spectrum observed without Q-lens. From the slope of the leading edge, the full width at half maximum (FWHM) of the resolution function was estimated to be 5.2 keV. This is in good agreement with the calculated kinematic broadening (5.7 keV), indicating that the effective energy resolution is mainly determined by the kinematic broadening. Using the stopping powers, the depth resolution was calculated to be 1.7 nm at the surface. This is better than the depth resolution of the TOF-ERDA setup mentioned above but several times worse compared to the resolution achieved by Dollinger *et al* using high-energy heavy ions

and the sophisticated magnetic spectrograph. In order to improve the depth resolution, trajectory simulations of the recoiled Li^+ ions were performed to determine the optimal voltage applied to the Q-lens. The ERDA spectrum observed with the Q-lens is shown by closed circles in Fig. 3. The leading edge becomes steeper compared to the result without the Q-lens, indicating improvement of the depth resolution. The leading edge was fitted to an error function. The obtained effective energy resolution at the surface is 1.6 keV, which represents the experimental energy resolution of the present setup. This energy resolution corresponds to the depth resolution of 0.5 nm at the surface. The obtained depth resolution is comparable to that achieved by Dollinger *et al* in spite of the much smaller equipment used in the present work.

Although the obtained depth resolution is excellent at the surface, it is known that the depth resolution deteriorates with depth due to the energy loss straggling as well as the multiple scattering. Actually the slope of the trailing edge (~ 295 keV) is much more gentle compared to the leading edge, indicating that the depth resolution deteriorates at the interface of LiF/Si. In order to estimate the depth resolution in a deeper region, Monte Carlo simulation for the ERDA spectrum was performed using the Corteo code [8]. Energy spectra of Li ions recoiled by 400 keV He ions from a thin Li layer (areal density 5×10^{13} Li atoms cm^{-2}) located at a depth x in Si were calculated for various x . In the simulation, the input parameters (scattering geometry, the acceptance angle of the spectrometer *etc*) were chosen to be the same as the measurements shown in Fig. 3. Figure 4 shows examples of the calculated spectra. The spectrum for $x = 0$ nm shows a rectangular shape and the width of the spectrum (5.7 keV) agrees with the calculated kinematic broadening (5.7 keV), indicating that the depth resolution at the surface is determined mainly by the kinematic broadening. With increasing depth, the spectrum becomes broader due to the multiple scattering and the energy loss straggling. The FWHMs of the calculated spectra are shown by open circles in Fig. 5. Using the stopping powers, the obtained FWHM can be converted to the depth resolution, which is shown by the vertical axis in the right hand side. Note that the calculated spectrum includes the effect of the kinematic broadening while the effect can be corrected using the Q-lens in the present ERDA system. Thus the depth resolution of the

present ERDA system is better than the result of the Corteo simulation.

The effect of the kinematic broadening was removed from the result of the Corteo simulation through deconvolution procedures. The resultant depth resolutions are shown by triangles in Fig. 5. Finally, taking account of the observed experimental energy resolution (1.6 keV), the depth resolution for the present setup was obtained. The obtained result was shown by closed circles in Fig. 5, which is about 0.5, 2 and 3 nm at $x = 0, 2$ and 5 nm, respectively.

The ERDA spectrum for LiF(2.8 nm)/Si calculated using the Corteo code is shown by a thin solid line in Fig. 3. Although the calculated spectrum agrees with the observed spectrum at the leading edge, there is a notable discrepancy at the trailing edge. The observed trailing edge is slightly gentle compared to the calculated spectrum. This indicates that the LiF layer is not uniform. Assuming an appropriate thickness distribution, the observed spectrum can be reproduced by the Corteo simulation as shown by a thick solid line. The obtained thickness distribution is shown in the inset of Fig. 3, which indicates that the LiF layer is rather uniform.

Finally we note that the information of the charge state distribution of recoiled Li ions is indispensable for quantitative analysis because only Li^+ ions can be measured in the present setup. The semi-empirical charge state distribution of Li ions passing through a carbon foil was given by Marion and Young [9]. According to their result, the Li^+ fraction is larger than 60% in a energy region from 235 to 550 keV with a maximum fraction of 66% at 400 keV. Although the charge state distribution may depend on the material, their result suggests that the Li^+ fraction is almost constant if we measure mainly the surface region using 400 keV He^+ as the probe like the measurement shown in Fig. 3.

4. Conclusion

A compact high-resolution ERDA system consisting of a small magnetic spectrometer and a small accelerator was developed for precise Li analysis. 200 - 400 keV He ions were used as the probe. This allows complete rejection of the scattered He ions from the Li spectrum. The recoiled substrate ions were also rejected and the background is

drastically reduced using a thin mylar foil placed in front of the focal plane detector. The residual background was almost the same level as the dark noise of MCP. The detection limit of Li was estimated to be less than 0.01 ML under a typical measurement conditions. The depth resolution at the surface was measured to be 0.5 nm. The depth resolution in the deeper region was estimated by the Corteo simulation. The estimated depth resolution is 2 and 3 nm at $x = 3$ and 5 nm, respectively. These depth resolutions are comparable to that achieved by Dollinger *et al* using a large magnetic spectrograph and a large accelerator, although their depth resolution does not deteriorate that fast with depth and their setup is not restricted to Li.

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Figure captions

Fig. 1 Schematic drawing of experimental setup for high-resolution ERDA.

Fig. 2 Examples of observed ERDA spectra for Li/graphite. The ions recoiled by the He^+ ions at 25° with an exit angle of 10° with respect to the surface plane were measured when 200 keV He^+ ions were incident on the sample. The spectra observed with and without a mylar foil are shown by closed and open circles, respectively. The measurement time was 1000 s for both spectra.

Fig. 3 Examples of observed ERDA spectra for $\text{LiF}(2.8\text{nm})/\text{Si}(001)$. The ions recoiled by the He^+ ions at 25° with an exit angle of 10° with respect to the surface plane were measured when 400 keV He^+ ions are incident on the sample. The spectra observed with and without Q-lens are shown by closed and open circles, respectively. The result of Corteo simulation for a uniform LiF layer of 2.8 nm thickness is shown by a thin solid line. The best fit result of Corteo simulation for a non-uniform LiF layer is also shown by a thick solid line. The inset shows the corresponding thickness distribution of the LiF layer.

Fig. 4 Energy spectra of Li ions recoiled from a thin Li layer (areal density 5×10^{13} atoms cm^{-2}) embedded in Si at various depths calculated using Corteo code. The incident ion, scattering geometry and the acceptance angle of the spectrometer are the same as the measurement shown in Fig. 3.

Fig. 5 The FWHMs of the Li peaks shown in Fig. 4 (open circles). The vertical axis in the right hand side shows the corresponding depth resolution. Estimated depth resolution after the correction of the kinematic broadening (triangles) and the result including the experimental energy resolution (closed circles) are also shown.

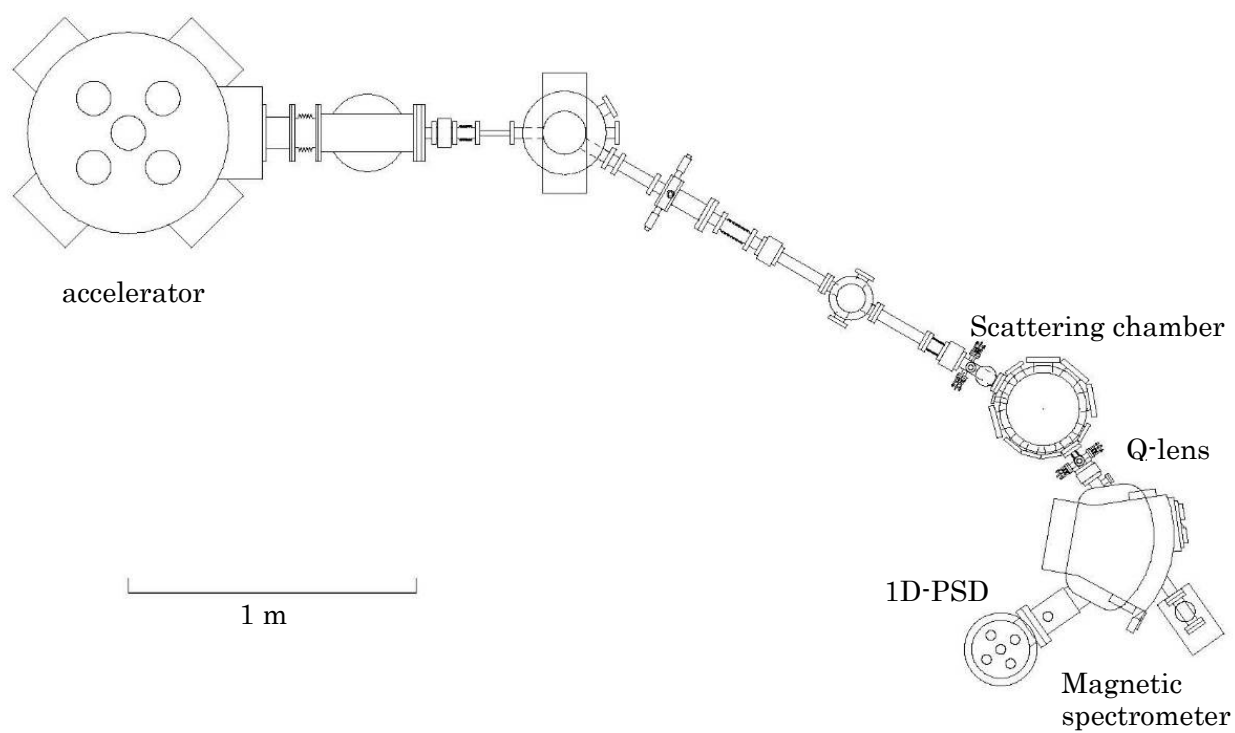


Fig. 1

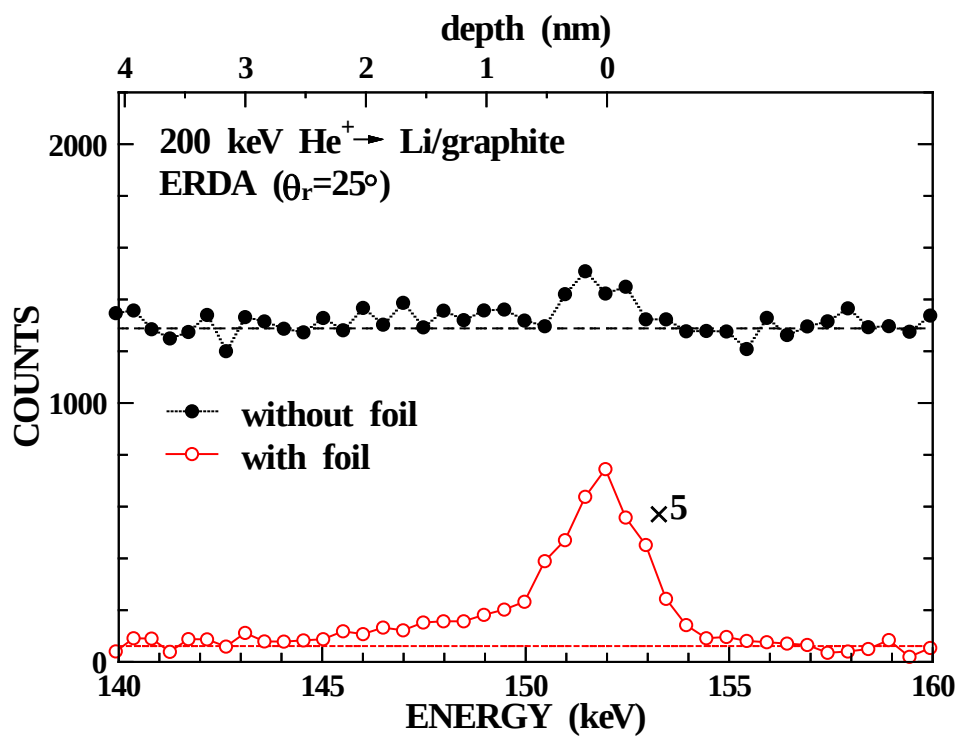


Fig. 2

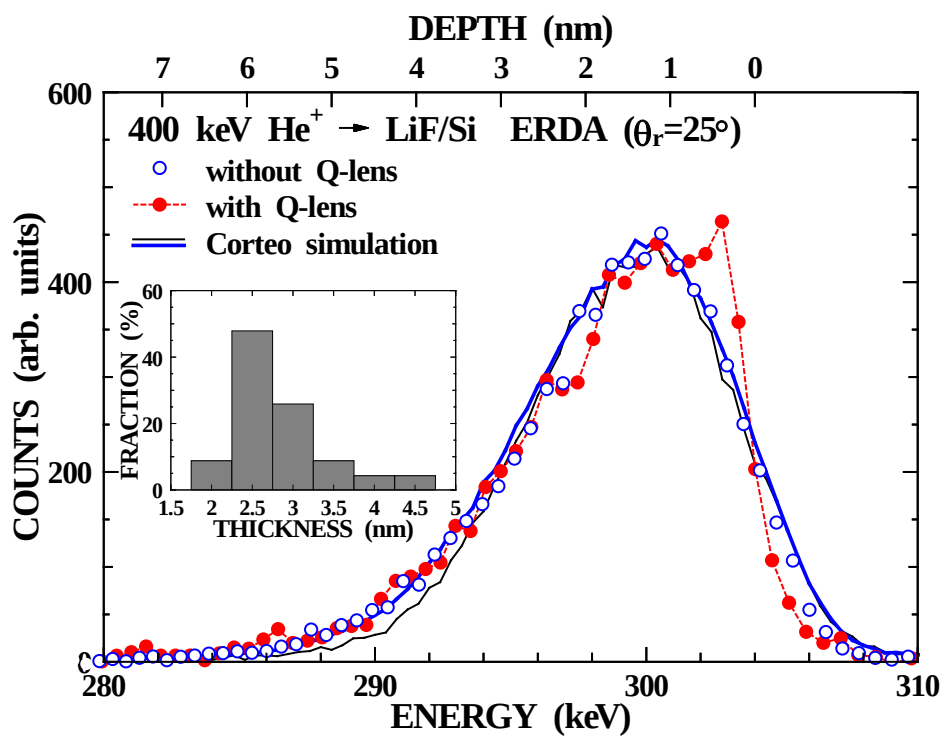


Fig. 3

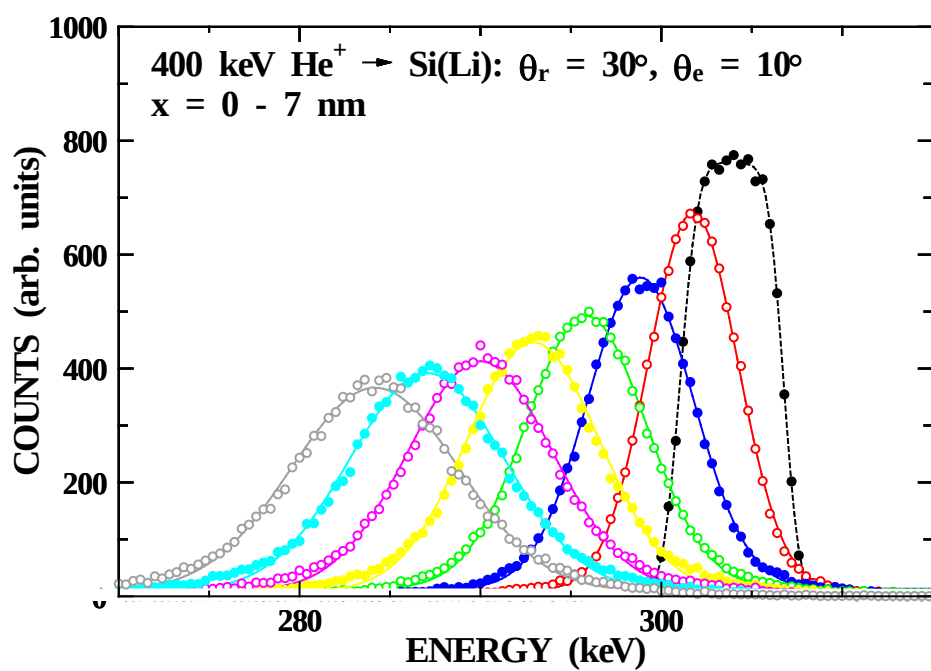


Fig. 4

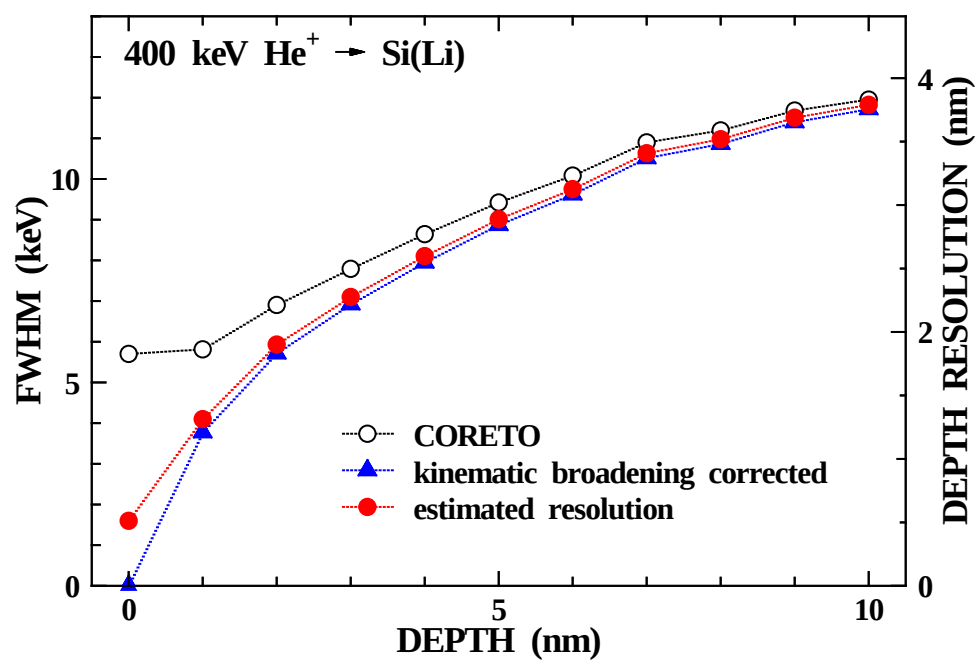


Fig. 5