Mem. SR Center Ritsumeikan Univ. No. 26, 37 (2024)

Lithiation Depth of Ge Electrode Studied by Hard X-Ray Photoelectron Spectroscopy

Shu Tsuchida[1], Ken-ichi Okazaki[2], Chengchao Zhong[1], Keiji Shimoda[3], and Yuki Orikasa[1]

1) *Department of Applied Chemistry, Ritsumeikan University, Kusatsu 525-8577, Japan*
2) *Research Organization of Science and Technology, Ritsumeikan University, Kusatsu 525-8577, Japan*
3) *Ritsumeikan Global Innovation Research Organization, Ritsumeikan University, Kusatsu 525-8577, Japan*

Germanium (Ge) is a promising negative electrode material for next-generation lithium-ion batteries because of its high theoretical capacity ($Li_{22}Ge_5$, 1624 mAh g^{-1}) relative to graphite (LiC_6, 372 mAh g^{-1}). In this study, the lithiation and delithiation reaction depth of the Ge wafer electrode was examined using soft and hard X-ray photoelectron spectroscopy (XPS).

A commercial Ge wafer was used for the working electrode after chemical etching to clean the wafer surface. Li foil was used for the counter electrode. The electrolyte was 1 mol dm^{-3} lithium bis(fluorosulfonyl)amide dissolved in *N*-methyl-*N*-propyl-pyrrolidinium bis(fluorosulfonyl) amide. Lithiation was performed by chronocoulometric method at 0.8 V vs. Li/Li^+ for one hour at 313 K. The cells were then disassembled in a glove box. The XPS measurements were performed using PHI Quantes (ULVAC-PHI) with monochromatic Cr and Al K_α radiations (5414.9 and 1486.6 keV, respectively). The pass energy was set to 69 and 26 eV, respectively. Dual-beam charge neutralization was applied to suppress sample charging. Binding energies were calibrated for the C 1*s* signal from adventitious carbon at 284.6 eV.

Figs. 1 (a) and (b) show the Ge 3*d* spectra of the electrodes acquired using Cr and Al K_α, respectively. The signal intensity at Cr K_α was much smaller than that at Al K_α because the photoionization cross section drastically decreases with increasing the incident X-ray energy. Fig. 1 (c) shows the Ge $2p_{3/2}$ spectra using Al K_α. The escaping depth of the photoelectron increases with increasing the incident X-ray energy and with decreasing the binding energy. The detection depth defined by $3\lambda\sin\theta$ (λ; inelastic mean free path of photoelectron, θ; take-off angle of photoelectron) was roughly estimated for metallic Ge using TPP-2M [1]. The detection depths of Figs. 1 (a-c) decreased from ~26 nm to ~3 nm. Fig. 1 indicated that the pristine wafer was covered by a thin oxide layer (< 3 nm in thickness). By lithiation (1d in Fig. 1), a small signal assigned to Li-Ge alloy was observed at a lower binding energy [2], suggesting that Ge in the alloy is negatively charged to some extent. The decreased peak intensity of Li-Ge may indicate the lower density of the alloy (volume expansion by lithiation) and/or the formation of a thick solid electrolyte interphase (SEI) layer, which covered the alloy layer (Fig. 1 (d)). The thickness of the SEI layer was considered to be ~9 nm. The SEI layer became thicker in the delithiated Ge wafer (> ~26 nm in thickness), and the Ge 3*d* and $2p_{3/2}$ signals could not be detected (1c in Fig. 1).

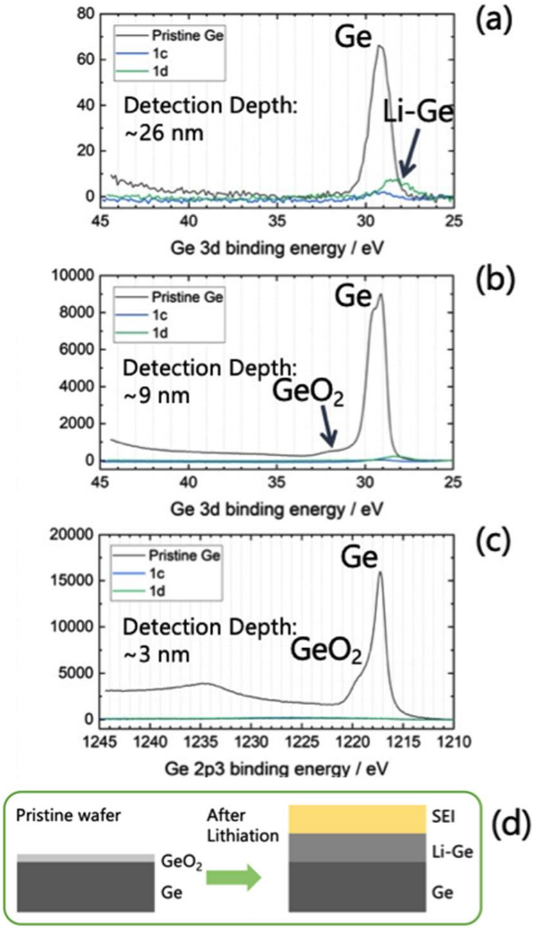

Fig. 1 (a-c) Ge 3*d* and $2p_{3/2}$ core-level spectra of the Ge electrode during the 1st discharge-charge cycle at different detection depths. (d) Illustration of lithiated Ge wafer.

References

[1] S. Tanuma *et al.*, *Surf. Interf. Anal.*, **1994**, *21*, 165.
[2] Z. Liu *et al.*, *J. Phys. Chem. C* **2021**, *125*, 13501.