Fundamental Properties for Enhanced Etching of Ge Surfaces in Water Assisted by Single Sheets of Reduced Graphene Oxide

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Metal-assisted chemical etching is an emerging technology for fabricating various three-dimensional nanostructures on a semiconductor surface for future electronic and optical devices. Thus far, our group has reported that a Ge surface in contact with noble metals, including Pt and Ag, is selectively etched in O_2-containing water [1]. However, it is extremely difficult to remove residual metallic particles on the processed Ge surfaces. To resolve this issue, graphene is used, which supposedly functions as a catalyst free from metals.

In this study, fundamental properties of graphene-assisted chemical etching, which is the preferential etching method for a Ge surface in contact with single sheets of reduced graphene oxide (rGO) in O_2-containing water were described. An rGO solution was prepared by chemical reduction of a GO solution [2] and spin-coated on a Ge(100) surface. The sample was immersed in O_2-containing water for 24 h. Figures 1(a) and (b) display the change in surface morphology of rGO sheet-loaded Ge upon immersion in O_2-containing water. The sheet thickness ranged from 0.8 to 1.2nm and single rGO sheets were well dispersed in Fig. 1(a). The Ge surface was preferentially etched under the rGO sheets in O_2-containing water (Fig. 1(b)) [3,4]. This enhanced etching did not occur using water without dissolved O_2 molecules, indicating that rGO-assisted chemical etching is mediated by an oxidant (O_2 molecules) in a solution (water). Next, the dependence of etching rate on water temperatures was investigated. The etching rate considerably depended on water temperatures (e.g., 1.9 nm/h at 22 °C and 15.1 nm/h at 48 °C, Fig. 1(c)). The Arrhenius plot from the data in Fig. 1(c) permitted the estimation of activation energy for this etching mode.

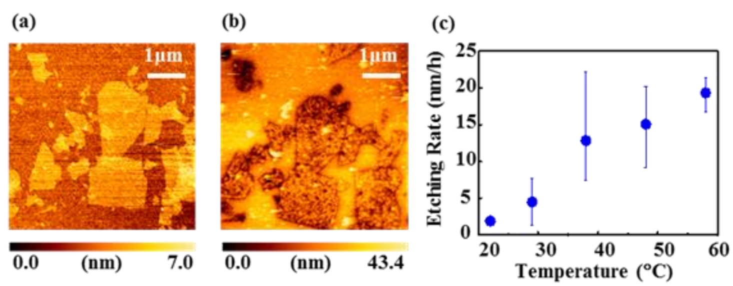

Figure 1. (a) AFM image of Ge surface loaded with rGO sheets. (b) After immersion into O_2-containing water. (c) Etching rate as a function of water temperature.

[1] T. Kawase et al., *ChemElectroChem*, **2** (2015) 1656.
[2] S. Park, J. An, I. Jung, RD. Piner, SJ. An, X. Li, A Valamakanni, RS. Ruoff, *Nano Lett.*, **9** (2009) 1593.
[3] T. Hirano, K. Nakade, S. Li, K. Kawai, K. Arima, *Carbon*, **127** (2018) 681.
[4] S. Li, K. Nakade, T. Hirano, K. Kawai, K. Arima, *Mat. Sci. Semicon. Proc.*, **87** (2018) 32.

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Supplementary information:

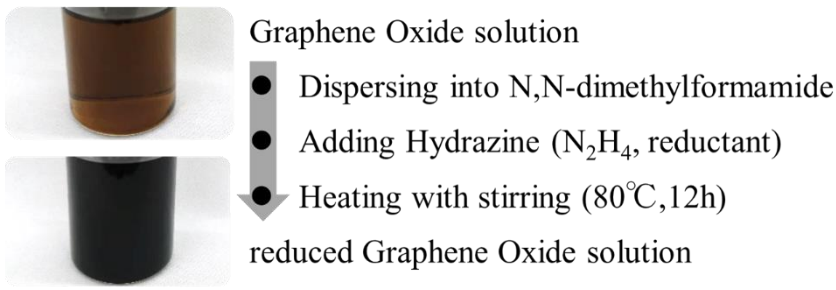

Figure S1. Schematic to obtain a colloidal suspension of rGO sheets.

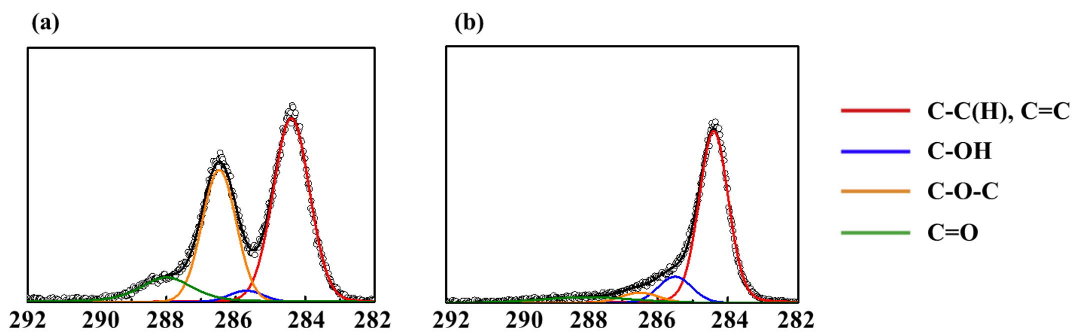

Figure S2. (a) and (b) show peak-fitted C1s XPS spectra before and after chemical reduction of graphene oxide (GO) films using hydrazine, respectively.

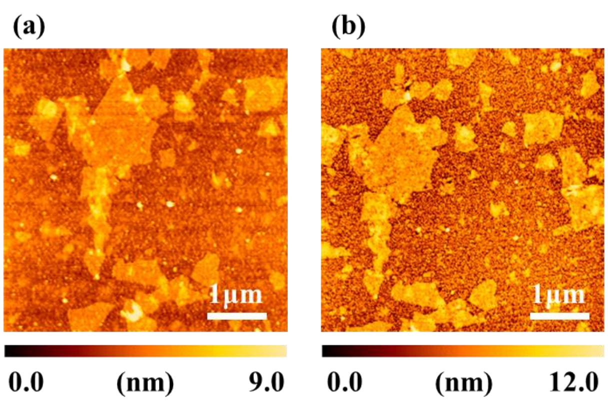

Figure S3. (a) AFM image of Ge surface loaded with rGO sheets. (b)After immersion into low-O_2-dissolved water. Neither pits nor etched hollows were observed.

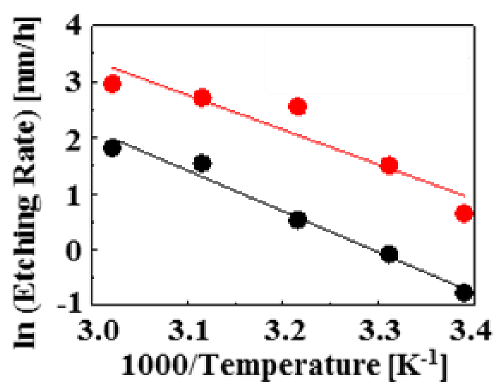

Figure S4. The Arrhenius plot for etching rates of Ge in O_2-containing water. Red and black plots were recorded for rGO sheets and on Ge not covered by rGO sheets, respectively.