



Investigation of reaction sequence occurring in graphene-assisted chemical etching of Ge surfaces in water

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ABSTRACT

This study aims to elucidate the reaction sequence of enhanced etching of Ge surfaces in water with the assistance of reduced graphene oxide (rGO) sheets. For this purpose, we performed *in situ* atomic force microscopy observations. After the immersion of a Ge surface loaded with dispersed rGO sheets into water, a water film was promptly intercalated at the rGO/Ge interface. First, the Ge surface along the outer edges of the rGO sheets was etched. Then, an etched hollow was formed beneath the entire rGO sheet. This is probably due to the chemical activity at not only the outer edges but also at the local edges of the small holes in rGO sheets. As etching of the Ge surface proceeded, the rGO sheet covering the etched bottom of a hollow was physically bent. We point out that the contact area between the wrinkled sheet and the Ge surface may decrease, affecting the etching rate.

1. Introduction

Graphene has potential to revolutionize materials science and electronic technologies because of its unique properties including ballistic transport up to room temperature, very high carrier mobility, and high elastic modulus. Edge-rich [1] and doped graphene [2] have also attracted considerable attention as catalysts for oxygen reduction reactions in fuel cells.

Recently, to enhance the etching of semiconductor surfaces in solution, researchers have shed new light on a unique property of graphene. Specifically, Kim et al. used chemical-vapor-deposition-grown graphene and patterned it on a Si substrate. They dipped this substrate into a solution containing HF and H₂O₂ to form either Si nanopillars or porous Si surfaces [3]. Our group has developed an approach by which Ge surfaces loaded with single sheets of reduced graphene oxide (rGO) are immersed in water. After removing the samples from the water, we observed the resultant surface morphologies by atomic force microscopy (AFM) in the air. And we found enhanced chemical etching properties catalyzed by rGO sheets in the presence of the dissolved O₂ molecules in water [4]. These studies demonstrate the potential of graphene as an attractive alternative to noble metals [5–8] as a catalyst to promote chemical etching and to control the structure of a semiconductor surface at the nanoscale.

However, in our preceding work [4], rGO-assisted chemical etching was found to have low etching rates. For the practical applications of this etching mode, it is of great importance to understand which factors

influence the etching rate. The durability, or the stability of the catalytic performance, of graphene sheets, is a relevant issue in this context. In addition, it is recognized that many kinds of molecules such as water and O₂ can be intercalated between a graphene sheet and a solid surface [9]. We imagine that the uniformity of the thin water film sandwiched at an interface between rGO and Ge greatly affects the etching rate. The motivation of this study is to elucidate the reaction sequence, or the elementary processes, of rGO-assisted chemical etching. For this purpose, we performed *in situ* AFM observations to monitor the changes in the rGO/Ge structures.

2. Experimental

2.1. Wet cleaning of Ge surfaces

P-type Ge(100) samples with resistivity in the range of 1–12 Ω cm were rinsed with semiconductor-grade ultrapure water with the specific resistance of 18.2 MΩ cm for 10 min and any organic contaminants were removed by treatment with an ultraviolet ozone generator for 10 min. Then, the samples were dipped into a dilute (0.5%) hydrofluoric acid solution (HF) for 1 min.

2.2. Formation of dispersed rGO sheets on Ge

A commercial, aqueous graphene oxide (GO) solution (5 mg/mL) was used as a precursor. The GO solution (0.8 mL) was mixed with

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ultrapure water (3.2 mL) and *N,N*-dimethylformamide (99.5%, 36 mL) and was subsequently reduced by hydrazine monohydrate (98.0%, 1.3 μ L) for 12 h in an oil bath at 85 °C to obtain a colloidal suspension of rGO sheets [10]. The solution with the obtained rGO was sonicated for 30 min and then centrifuged at 4000 rpm for 30 min to remove aggregates. Some droplets of the black suspension including rGO sheets were put on a Ge surface using a micropipette and were spin-coated at 250 rpm for 5 s then at 2000 rpm for 30 s to form dispersed rGO sheets.

2.3. AFM observations

A commercial AFM setup (SPI3800N/SPA-400, Hitachi High-Technologies Corporation) equipped with a liquid cell filled with ultrapure water was used to observe the Ge samples with rGO sheets. The sample was immersed in water at room temperature and the Si cantilever with a resonant frequency of 110 kHz and a spring constant of 0.09 N/m was brought near the Ge surface. After immersing the sample into water, it took about 40 min to finish approaching a cantilever to

the sample surface. Then, the time was noted, which is defined as the immersion time hereafter. The cantilever was scanned across the surface in contact mode. It was assumed that water in the liquid cell exposed to an air included the dissolved O₂ concentration of 7–9 ppm. The AFM setup was also operated in tapping mode in air using a Si cantilever with a resonant frequency of 300 kHz and a spring constant of 26 N/m.

3. Results

Fig. 1(a) is an AFM image of a Ge surface with spin-coated rGO sheets that was taken in air. This image clearly shows that the rGO sheets were well dispersed. Fig. 1(b) shows cross-sectional profiles along lines A-A' and B-B' indicated in Fig. 1(a), thus indicating that the rGO thickness is \sim 1.5 nm. Fig. 1(c) is an AFM image of the Ge

surface with dispersed rGO sheets that was taken in water. Fig. 1(d) shows cross-sectional profiles along the lines C-C' and D-D' indicated in Fig. 1(c). The measured rGO sheet thicknesses of the C-C' and D-D' lines

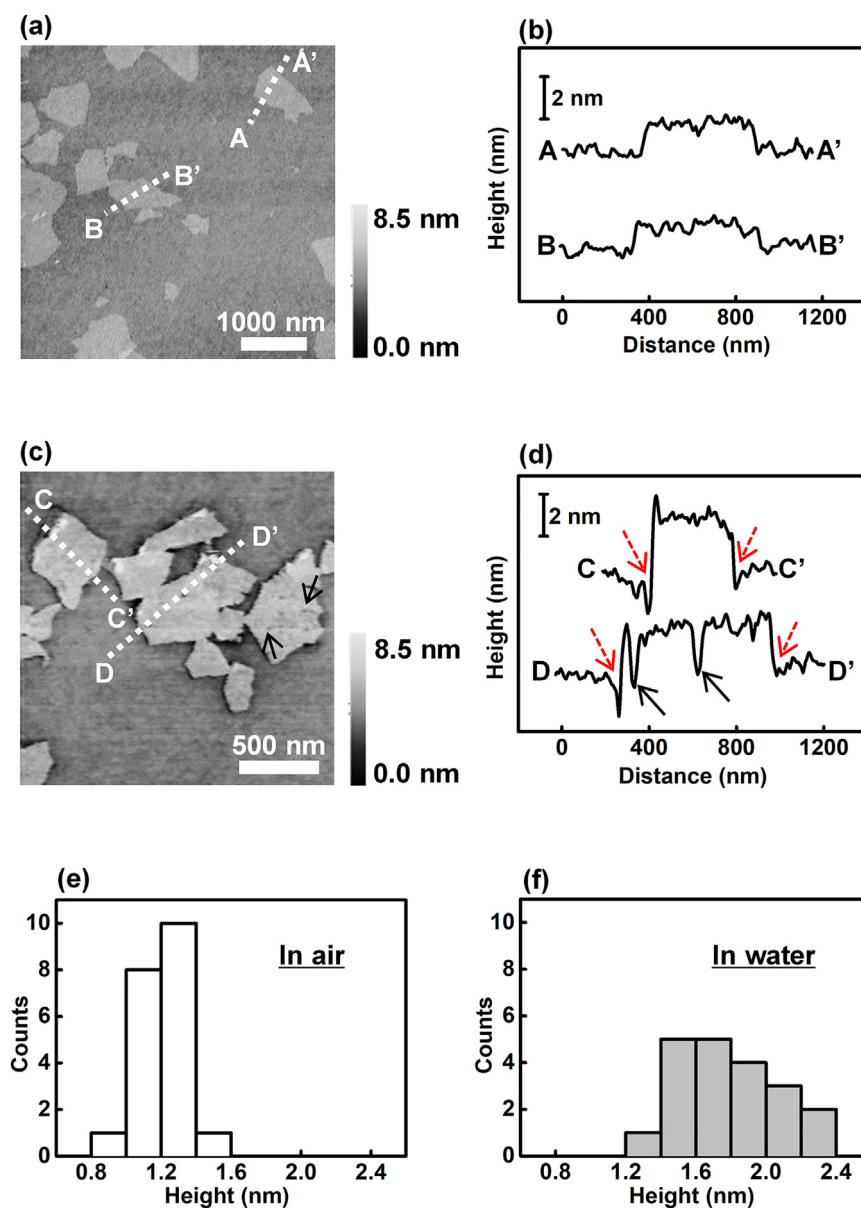


Fig. 1. AFM images of a Ge surface loaded with dispersed rGO sheets. (a) Images taken in air and (b) the corresponding cross-sectional profile along lines A-A' and B-B' in (a). (c) Images taken in water at the immersion time of 2 h. The gray scale in (c) was adjusted to be consistent with that in (a). (d) Cross-sectional profiles along lines C-C' and D-D' in (c). (e) and (f) show the frequency distributions of measured rGO thicknesses in air and in water, respectively.

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