Porous Ge based Electric Double Layer Capacitors with High Compatibility for Low Threshold Voltage Diode Rectifiers

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Abstract. The final goal of this study is to develop all-Ge-based energy harvesting modules consisting of mechanical generators, rectifiers, capacitors and power managing digital circuits. To make basis for the development of modules, we focused on development of the Ge electrodes for electric double layer capacitors (EDLC). Firstly, to establish a method to make high surface area Ge electrodes, we studied surface etching of the Ge(100) substrates in the acid solution. We found that the substrates with higher dopant concentration forms smaller size micro-pores with higher area density that leads to higher surface area. Secondly we studied stability of Ge in the ionic liquid (IL) electrolyte by ac impedance measurements. The impedance plots verified that Ge is reactive in IL electrolyte, thus not appropriate for electrodes without surface modification. Finally we oxidized Ge surface and tested the stability again. The impedance plot of the surface-oxidized Ge showed little reaction, proving that we succeeded to improve the surface stability.

1. Introduction

The energy harvester modules have been collecting attention as an on-site power generator for micro devices. Generally components of the energy harvester modules such as mechanical generators, rectifiers, capacitors and power managing digital circuits are fabricated separately and integrated at last. If the components are made of the same material, we can fabricate those on a single substrate simultaneously. Then manufacturing cost and size of the modules can be reduced. Also, its parasitic capacitance and leak current will be decreased.

Ge should be a promising material because it is known for the established MEMS fabrication processes and lower threshold voltage than that of Si, which enables to make low power consumption diode circuit. Moreover, micro porous can be made on Ge by etching in acid solution. This enables us to prepare large surface area electrodes for making large capacity EDLCs. However, so far the etching conditions to make large surface area were not understood. In addition there has been no report of Ge as electrodes of EDLCs.

In this study, we challenged to make basis for the development of Ge electrodes for EDLCs and investigated two electrochemical properties of Ge. At first, we investigated the relationship between the porous structure and the doping level of a Ge(100) substrate in acid solution to find out the etching conditions to realize large surface area. Then we evaluated the stability of Ge electrodes in an ionic liquid BMIM-AC electrolyte by observing chemical reaction at the electrode/electrolyte interface.
2. Experiment
In this study, the ionic liquid is adopted as an electrolyte because it has larger chemical window (2~4 V) than conventional electrolytes such as \( \text{H}_2\text{SO}_4 \) (1 V) [1].

2.1. porous structure formation
We prepared three Sb-doped one-side polished Ge(100) substrates with different doping levels \( 3.0 \times 10^{14}, 3.5 \times 10^{15}, \text{and} \ 1.0 \times 10^{16} \text{atm/cm}^3 \). The substrates were n-type because it suppresses hole-mediated chemical reaction and limits number of reaction sites and avoids incorporation of micro-pores. The size is \( 2 \times 2 \text{ cm}^2 \) square with thickness of 500 \( \mu \text{m} \). The Ge substrate was etched by HCl solution \([\text{HCl}:\text{CH}_3\text{CH(OH)CH}_3:\text{H}_2\text{O} = 1:1:6]\) in a double cell etching setup (Fig. 1) [2,3]. Etching was conducted for 1 h by flowing current of 2.5 mA/cm\(^2\) between Pt anode and cathode. A Ge substrate on the current flow path undertakes electrochemical reactions [4].

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\begin{align*}
\text{Ge} + \text{H}_3\text{O}^+ + e^- & \rightarrow \text{GeH} + \text{H}_2\text{O} & (1) \\
\text{H}_3\text{O}^+ + \text{GeH} + e^- & \rightarrow \text{Ge} + \text{H}_2 + \text{H}_2\text{O} & (2)
\end{align*}
\]

on the anode side, and

\[
\text{Ge} + n\text{H}^+ + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{GeO}_3 + 4\text{H}^+ + (4-n)e^-
\]

on the cathode side, respectively. \( \text{H}_2\text{GeO}_3 \) solves into the solution and pore is formed on the cathode side of the Ge surface. [3,4]

2.2. Stability in IL
In order to investigate chemical stability of the Ge substrate in IL, we constructed the EDLC consisting of Ge electrodes, and conducted ac impedance measurements. We used 1-Butyl-3-methylimidazolium acetate (BMIM-AC) as an IL electrolyte because that does not contain reactive fluorine. Additionally, comparison was made for Ge with oxidized surface layer prepared by thermal oxidization at 550 °C under \( \text{O}_2 \) pressure of 0.1 MPa for 1 h [5].
3. Results and discussion

3.1. Porous structure formation

Figure 2 shows plan [(a) – (c)] and cross-sectional [(d)-(f)] views of scanning electron microscopy (SEM) images of surface of Ge(100) substrates with different dopant levels after the etching. From these observations, it was verified that porous structure strongly depends on the dopant levels. As shown in Figure 2 (a), for the lowest dopant level (3.0×10^{14} atm/cm^{3}), etching uniformly takes place on the surface and fails to form porous structure. In cross-sectional view [Fig.2 (d)], we could not see porous structure. With increase in the dopant levels, etching becomes less uniform and anisotropic (faster etching along [100] direction), leading to formation of the micro-porous structure. Interestingly, size and distribution of the micro-porous structure depends on the dopant level. As shown in Figure 2 (b), large cross-shaped macro-pores of about 70 × 70 μm^{2} and small micro-pores of about 10 × 10 μm^{2} appeared for 3.5×10^{15} atm/cm^{3}. As shown in Figure 2 (e), the pore has cone-shape, indicating that etching occurred selectively along depth. In contrast small micro-pore of less 5 × 5 μm^{2} appeared densely for 1.0×10^{16} atm/cm^{3} together with large micro-pore of about 20 × 20 μm^{2}. In Figure 2 (f), we can see that many micro-pores were created vertically. This fine and dense porous structure is adequate to prepare large surface area Ge electrodes for EDLCs. Note that the formation of the cross-shaped pore may be ascribed to the intrinsic crystal anisotropy and consequential anisotropic career density that causes a shortage of the doped career partly [3].

![Figure 2](image_url)

**Figure 2.** SEM images of pores on the n-type Ge substrate with different Sb doping amount: (a-c) plain views, and (d-e) cross-sectional views

3.2. Stability in IL

To evaluate adequacy of Ge as an electrode of the EDLC, we implemented ac impedance measurements (0.1 Hz ~ 1.0×10^{6} Hz) of the Ge(100) substrates (dopant density ≳ 1.0×10^{16}) with and without surface oxide layer in BMIM-AC. Figure 3 shows obtained impedance plots. Typical impedance plot of the electrode/electrolyte interface in the EDLC in the inset indicates that the plot shows vertical straight line at the lower frequency region (on the right) if the electrical double layer is formed at the interface [6]. As shown in Figure 3 (a), in contrast, a plot of pure Ge bended downward with decrease in the frequency, indicating that chemical reaction took place at the interface. Thus pure Ge is not suitable as an electrode of EDLCs if IL is used. To solve this problem, we challenged to stabilize Ge surface by growing GeO_{2} layer by considering that generally oxides are stable compounds due to their large formation energy. Actually the impedance plot of the surface-oxidized Ge showed almost straight line for entire frequency range.
range. Thus significant improvement in the stability against IL by surface oxidization is verified. Looking at the plots closely, we noticed that the plots intersect with horizontal axis at $Z_{re}$ of between 500 and 1000 $\Omega$ [Fig. 3(b)]. This indicated that even heavily doped Ge (0.029 ~ 0.054 $\Omega \cdot$ cm) still suffers from high resistance. We believe that ongoing experiments will establish innovative method to reduce resistance.

In this study, porous structure formation and oxidizing Ge were conducted separately. In next study, we fabricate low resistive Ge electrode included porous structures and an oxidation layer. Then we will investigate the characteristics of the EDLCs.

![Figure 3. Impedance characteristic of the Ge and Ge oxide in BMIM-AC.](image)

4. Conclusion
We investigated the relationship between porous structures and the doping levels. We also investigated stability of Ge for IL. The doping levels strongly affects porous structure formation in acid solution. At the high doping level ($1.0 \times 10^{16}$ atom/cm$^3$), we got micro-pores densely. So high doping condition is suitable for preparing large surface area on Ge substrate. Ge oxide layer showed stability for IL. By comparing pure Ge, we could see the improvement of stability in impedance plots. These results gave research direction to MEMS production of Ge based EDLCs. This study will finally open the way for all-Ge-based energy harvesting modules.

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