Investigation of Interface between Ge Electrodes and Ionic Liquid Electrolytes for Electric Double Layer Capacitors

R.M Abeysinghe[1], H. Oguchi[2] and H. Kuwano[1]
[1]Division of Nanosystems, Department of Robotics, Tohoku University, 6-6-01, Aramaki-Aoba, Aoba-ku Sendai, Miyagi 980-8579, Japan.
[2] AIMR, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan.

E-mail : maduka@nanosys.mech.tohoku.ac.jp

Abstract. This study discusses novel way of use of ionic liquids to develop Ge-based electrodes for electric double layer capacitors (EDLC). We found that ionic liquids change their electrochemical properties depending on the amount of the absorbed water. Wet ionic liquids work as solvents to dissolve Ge and make porous structures, whereas dry ones work as electrolytes of the EDLCs. The former property was used to increase surface area of the electrodes which is desired to increase the capacity of EDLCs. This method showed another advantage in contrast to the dry ionic liquids; wet ones could fill the complex Ge pores in parallel to porous structure formation. Finally, after porous formation, we dried the ionic liquid at 100 °C and prepared the EDLCs composed of Ge porous electrodes. Cyclic voltammetry and impedance measurements indicated that the obtained devices can work as EDLCs.

1. Introduction

Semiconductor-based electric double layer capacitors (EDLC) have been collecting attention as energy storage devices for integrated micro devices consisting of sensors, diodes, actuators *et al* [1]. In this context we have challenged to fabricate the world first Germanium (Ge)-based EDLCs [2] compatible with micro-fabrication processes. Moreover, Ge-based EDLCs will enable integration with Ge diodes which has lower rectification threshold voltage than Silicon (Si).

In the previous research we succeed in obtaining large surface area Ge electrodes with micro porous structure preferable to increase capacity of the EDLCs by etching Ge in acid solutions. Then we fabricated the EDLCs using ionic liquid (IL) electrolytes [2] to take advantage of its higher decomposition voltage, which leads to higher energy storage. However large current observed in a cyclic voltammetry (CV) indicated unfavourable chemical reactions at the interface of Ge/IL (Fig.1). In addition, we noticed that IL did not fill in the porous structure as indicated by contact angle of 48.8° (Fig.2(a)) and Scanning Electron Microscope (SEM) images (Fig.2(b)).

The primary purpose of this study is to stop chemical reactions at the interface of Ge/IL based on understanding of the chemical reaction origin, and the secondary purpose is to develop proper method to fill in the pores by the IL. For these purposes firstly we studied the importance of the absorbed water contained in the IL. After that by uniquely controlling water amount dissolved in the IL electrolytes, we solved the both issues mentioned above.
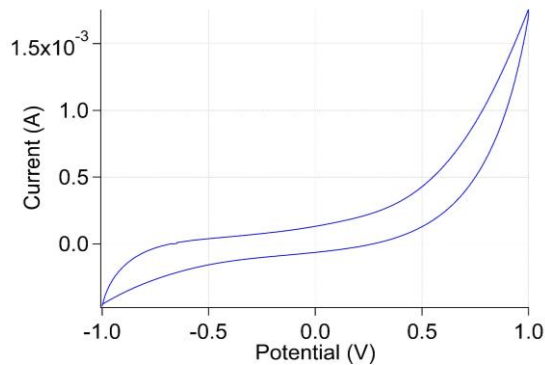
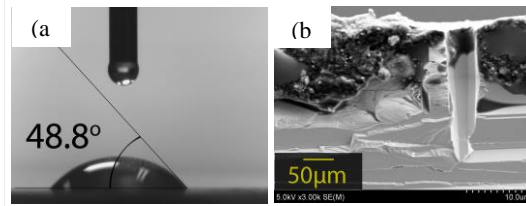**Figure 1. A** CV curve obtained with scanning rate of 0.01V/sec

Figure 2. (a) Contact angle measurement of an IL droplet on a porous Ge substrate. (b) A cross-sectional SEM image of the Ge micro porous structure. Black part corresponds to the IL. A pore on the right was only partially filled by IL.

2. Experiment

In this study we used one-side polished Sb-doped n-type (100)-oriented Ge wafers with resistivity of 5 - 20 mΩcm. The wafers were rinsed using Isopropyl Alcohol (IPA) in ultraviolet cleaner for 20 mins to remove contamination. On the rough side of the wafer, we deposited Ti adhesion layer (thickness: 20nm) and Pt (thickness: 200nm) electrode using Sputtering (EIKO Sputtering) method. Then samples were diced into 9.5×9.5 mm^2. For these samples, we tried to form Ge porous structure using experimental setup shown in Fig.3. By applying constant voltage between two Pt electrodes, chemical reactions occurred at the interface between the ionic liquid and Ge substrate. The distance between two electrodes was set to be 1mm. Electrochemical reactions were studied using electrochemical measurement system (VersaSTAT, version 4.0, Princeton Applied Research). Surface morphology was observed using scanning electron microscopy (HITACHI SU-70).

3. Results and Discussion

3.1. Investigation of the chemical reactions origin

Guessing from reported reaction between Ge and water [3], the chemical reaction observed in our previous experiments can be attributed to the water absorbed in the IL.

$$Ge + 2H_2O \rightleftharpoons GeO_2 + 4H^+ + 4e^- \qquad (1)$$

To confirm our guess, for ionic liquid EMIM-IM with different amount of absorbed water, we implemented CV measurements using the setup shown in Fig.3. The amount of the absorbed water was changed by pumping and heating the as-supplied EMIM-IM in the vacuum chamber with back pressure of 2×10^{-4} Pa. As-supplied EMIM-IM showed the current (at 1V, 10×10^{-6} A) attributed to the reaction between the ionic liquid and Ge (Fig.4). On the other hand, current decreased after pumping (at 1V, 3×10^{-6} A). Pumping and heating treatment further decreased the current value (at 1V, 1.5×10^{-6} A). These observations clearly indicated that water is the dominant factor for the chemical reactions.
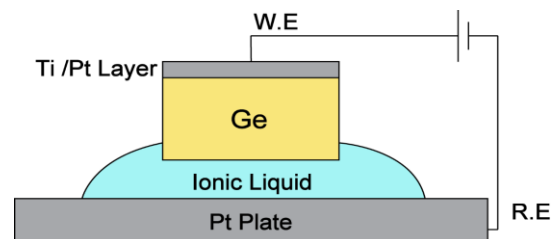

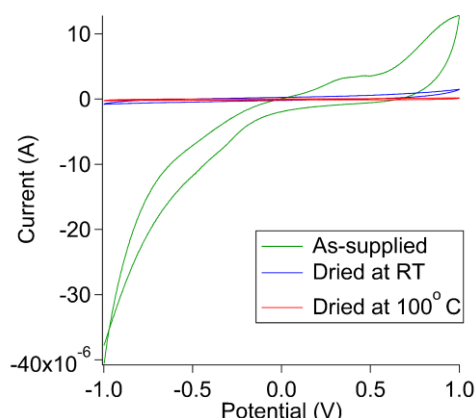**Figure 3.** Schematics of electrode – electrolyte – electrode three layer structure.

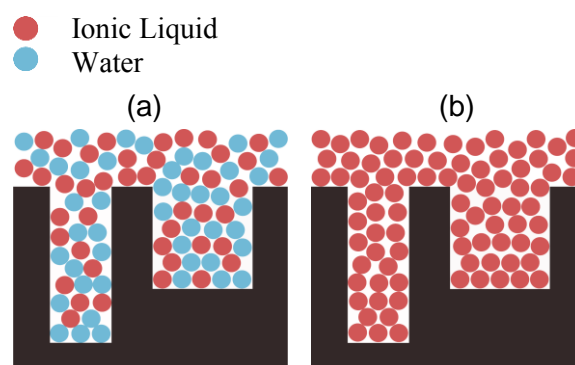**Figure 4.** Comparison of CV curves for differently prepared BMIM-PF$_6$.

Figure 5. IL drying procedure (a) IL with water (As-supplied), (b) After completely dried up at 100°C in vacuum

3.2. Development of new porous formation method

Based on the understanding that absorbed water in the IL reacts with Ge, we proposed an interesting method to form and fill in the porous structures in parallel. The method forms porous structure by use of IL with water (Fig.5(a)). Then the IL is dried up at 100°C in vacuum (Fig.5(b)). In this way, porous structure is obtained and filled by IL without water, which works as an electrolyte for EDLCs.

To verify our idea, we conducted Ge porous formation in air by using the as-purchased ILs. In addition, to find the appropriate conditions, we controlled three variables; IL species, voltage, and elapsed time. SEM observations (not shown) indicated that among the three different ILs which were used in the experiment (BMIM-PF$_6$, BMIM-AC and EMIM-IM), EMIM-IM has the highest capability to form the porous structure. Moreover, larger voltage and longer elapsed time increase penetration depth of the pores.
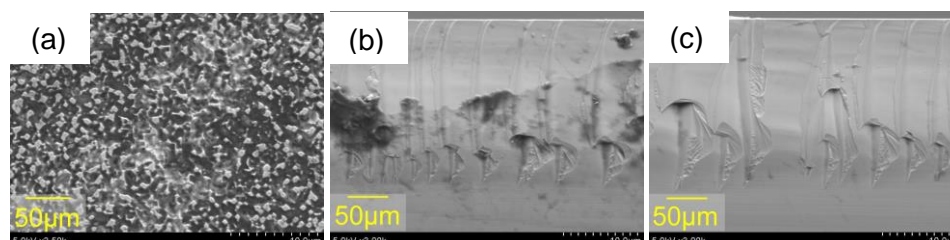

Figure 6. SEM images of the Ge after porous formation at 3V for 60hrs, (a) Surface morphology and Cross section of (b) before clean up (c) after clean up.

Based on the above results we formed the largest and uniform porous structures by applying 3V for 60 hours in air (Fig.6(a)). Furthermore the cross-sectional SEM image showed that the ionic liquid appeared as black part penetrated into the deepest part of the pores (Fig. 6(b), (c)), indicating that the porous structure can be filled by the ionic liquids using this method. Note that the black part was confirmed as the EMIM-IM from the fact that it was removed by cleaning up the sample using ethanol (Fig.6(c)).

To get EDLC operation, we dried the EMIM-IM remained in the pores at 100 °C for more than 24 hours. The cyclic voltammetry (Fig.7(a)) and impedance plots (Fig.7(b)) before and after the drying treatment clearly changed the behaviour. After the drying treatment, CV current reduced and Impedance plot was elongated along the vertical axis (imaginary part of the impedance Z_{im}), indicating that the chemical reaction was almost stopped at the Ge/IL interface.
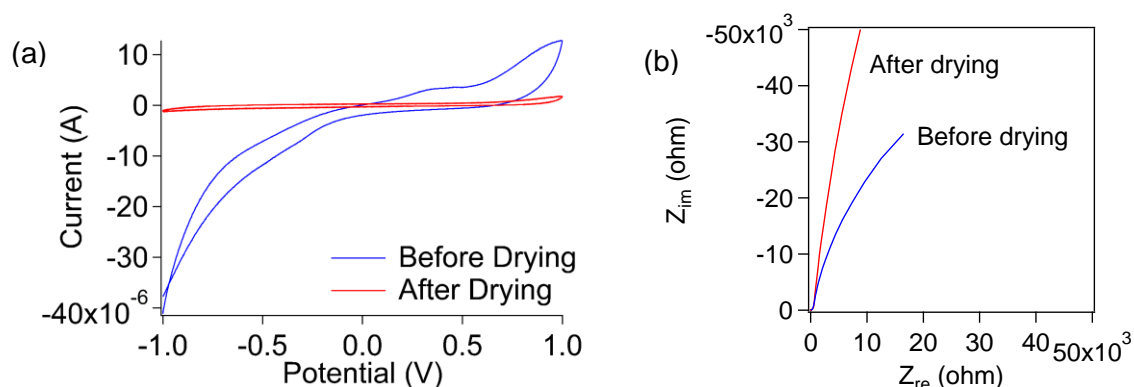
Figure 7. (a) CV curves and (b) Impedance plots obtained before and after drying treatments.

Finally, capacity of the EDLCs was evaluated for the Ge electrode with porous structures filled by dry IL. Increase in the current value of CV curves (Fig. 8) obtained before and after Ge porous formation found that we succeeded in increasing the capacity of the Ge-based EDLCs by using the Ge electrode with micro porous structures. The increase is, however, not so much as we expected. Possibly straight and shallow pores could not increase surface area of the Ge effectively. In addition, water could be trapped in the pore and drying of the IL was not complete.
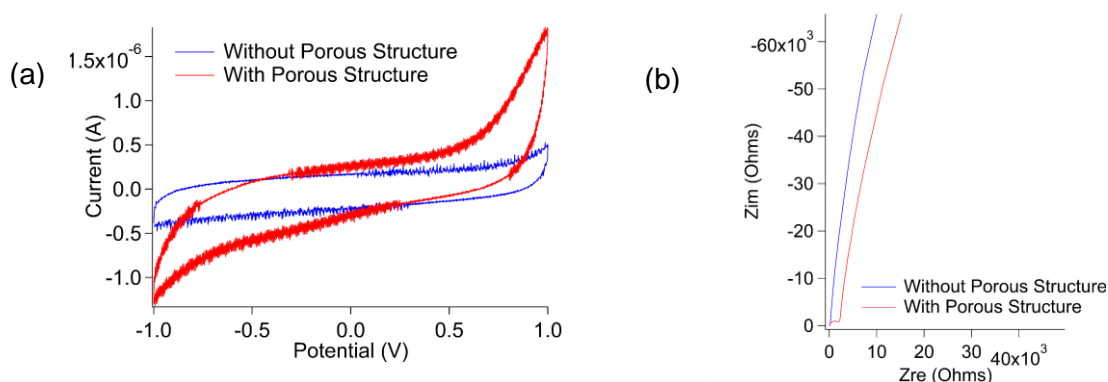

Figure 8. (a) CV curves and (b) Impedance plots before and after porous structure formation.

4. Conclusion

We verified that water amount contained in the IL is one of the dominant factor of the chemical reactions at the Ge/IL interface. In addition, we revealed that Ge micro porous structure need special treatment to be filled by the IL electrolyte. Based on these facts, we proposed a new method; forming and filling the micro porous structure simultaneously by controlling the absorbed water in IL. Using this method we succeeded in preparing Ge electrodes with a porous structure filled by IL. Moreover, by drying the IL filling the porous structures, chemical reactions were almost suppressed, indicating the promise of the proposed method for Ge-based EDLCs.

References

[1]   Beom-Jin Yoon, Soo-Hwan Jeong, Kun-Hong Lee, Hyung Seok Kim, Chan Gyung Park and Jong Hun Han, 2004 "Electrical properties of electrical double layer capacitors with integrated carbon nanotube electrodes," *Chemical Physics Letters,* Vol **388** pp 170–174.
[2]   A. Sekiguchi, M. Hara, H. Oguchi and H. Kuwano, 2014 "Porous Ge based Electric Double Layer Capacitors with High Compatibility for Low Threshold Voltage Diode Rectifiers," *Journal of Physics: Conference Series,* Vol **557**, *Conf.*1.
[3]   Tatsuya Kawase, Atsushi Mura, Katsuya Dei, Keisuke Nishitani, Kentaro Kawai, Junichi Uchikoshi, Mizuho Morita and Kenta Arima, 2013 "Metal-assisted chemical etching of Ge(100) surfaces in water toward nanoscale patterning," *Nanoscale Research Letters,* chapter 8 p 151.