A MICRO-STRUCTURED SI-BASED ELECTRODES FOR HIGH CAPACITY ELECTRICAL DOUBLE LAYER CAPACITORS

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Abstract. We challenged to make basis for Si electrodes of electric double layer capacitors (EDLC) used as a power source of micro-sensor nodes. Mcroelectromechanical systems (MEMS) processes were successfully introduced to fabricate micro-structured Si-based electrodes to obtain high surface area which leads to high capacity of EDLCs. Study of fundamental properties revealed that the micro-structured electrodes benefit from good wettability to electrolytes, but suffer from electric resistance. We found that this problem can be solved by metal-coating of the electrode surface. Finally we build an EDLC consisting of Au-coated micro-structured Si electrodes. This EDLC showed capacity of 14.3 mF/cm$_2$, which is about 530 times larger than that of an EDLC consisting of flat Au electrodes.

1. Introduction

Micro-sensor nodes have been developed to construct a sensor network to realize social monitoring system. One of the key components of the micro-sensor nodes is an energy source, and an electric double layer capacitor (EDLC) is anticipated to be a suitable device. If we can fabricate EDLCs on a single chip using microelectromechanical systems (MEMS) processes, manufacturing accuracy and degree of designing freedom should be increased. Thus we came up with fabricating EDLCs using MEMS compatible Si. Si has, however, never been studied as a material for electrodes of EDLC, and little is known for its behavior in EDLC applications.

Thus in this study, firstly we demonstrated fabrication of high surface area electrodes by MEMS processes, and investigated fundamental properties of the electrodes. Then we fabricated EDLCs consisting of Si electrodes, and evaluated device performance.

2. Experiment

To obtain high surface area Si electrodes by MEMS processes, we tested three ways: deep reactive ion etching (DRIE), anode oxidization, and glancing angle deposition GLAD. The anode oxidization is

conducted for p-type Si(100) substrates with resistivity of 1 - 10 Ωcm. The surface of the substrate was etched in the acid solution containing 50% HF and ethanol by flowing current of 10 mA/cm^2 for 60 min. GLAD is a method to deposit a film by impinges atomic or molecular flux to the substrate from an oblique angle [1]. Figure 1 shows a schematic of the GLAD setup used in this study. The GLAD takes place on the side wall of the micro-pillars that makes an almost right angle with depositing atoms. A Cr adhesion layer and then an Au nano/micro-rods were deposited while rotating a sample stage at 20 rpm at room temperature.

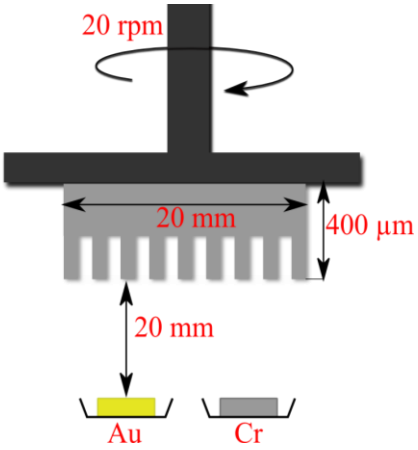

Figure 1: A schematic of the GLAD physical vapor deposition system including detailed information of deposition.

Wettability of the Si electrodes to electrolytes was studied by contact angle measurements. Micro structures were observed by scanning electron microscopy (SEM). Electrical resistivity of the Si electrodes was measured by an ac impedance method. Capacity of the EDLCs were evaluated by observing electrode potential during discharging.

3. Results and discussion

To demonstrate fabrication of high surface area Si electrodes by MEMS processes, we conducted microfabricaion on the Si(100) substrates. Figure 1(a) shows a scanning electron microscopic (SEM) image of the Si electrode obtained after DRIE. Densely and periodically aligned Si micro-pillars (50 μm width × 50 μm depth × 300 μm height, 50 μm gap in between) confirm high surface area. In addition, fine needle-like structures observed at the bottom of the pillars may further increase the surface area. Then, in pursuit of further increase in the surface area, we tried to construct more complicated micro structures using anode oxidization method in which electrochemical surface etching takes palce by flowing current of 1.2 mA/cm^2 for 60 min in a solution of HF : ethanol = 1 : 2. As a result, micro-porous of 1.5 μm-diameter and 15μm-height was obtained on the entire surface [Fig. 1(b) and (c)]. Calculation indicates that surface of the micro-porous Si electrodes has about 30 times higher surface area than that of flat Si electrodes.

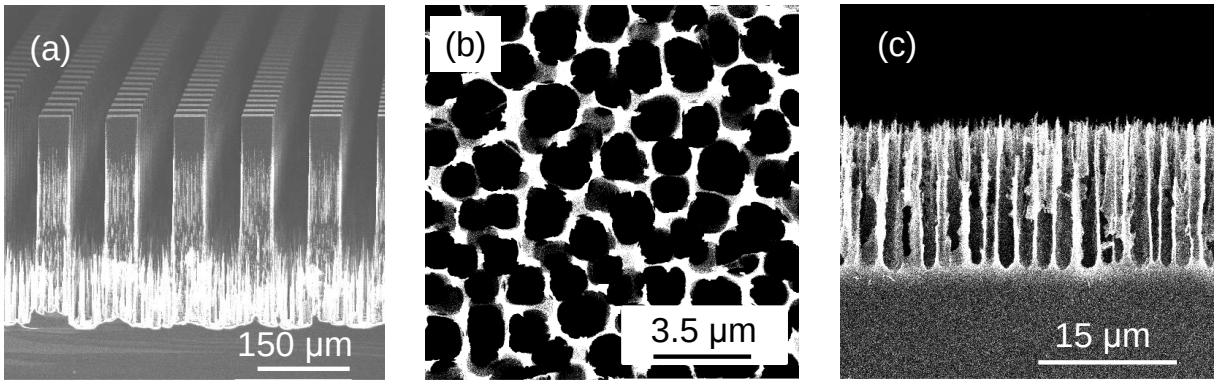

Figure 2. (a) A SEM image of a Si electrode obtained after DRIE. (b) Plain view and (c) cross-sectional SEM images of micro-porous structures.

To judge capability of Si as electrodes of EDLCs, we investigated resistance and wettability to electrolyte. The resistance was measured for the EDLC-type setup consisting of Si electrodes or Pt electrodes. $BMIMPF_6$ was used an ionic liquid electrolyte. Figure 3(a) shows impedance plots of Si and Pt electrodes. The plots intersect with real part of the impedance (horizontal axis) at 200 Ω and 0 Ω for Si and Pt, respectively. This indicates that Si is very resistive and not suitable as electrodes without modification. The wettability was evaluated by contact angle measurements for Si substrates without and with micro-porous on the surface. Figure 3 shows the side view images of water droplet on Si (b) without and (c) with micro-porous. Contact angle for (b) and (c) are 76.3° and 7.4°, respectively, clearly illustrates better wettability for the latter. Thus the micro-porous Si is good for electrodes because electrolytes will easily diffuse into the micro-porous during charging/discharging of EDLCs.

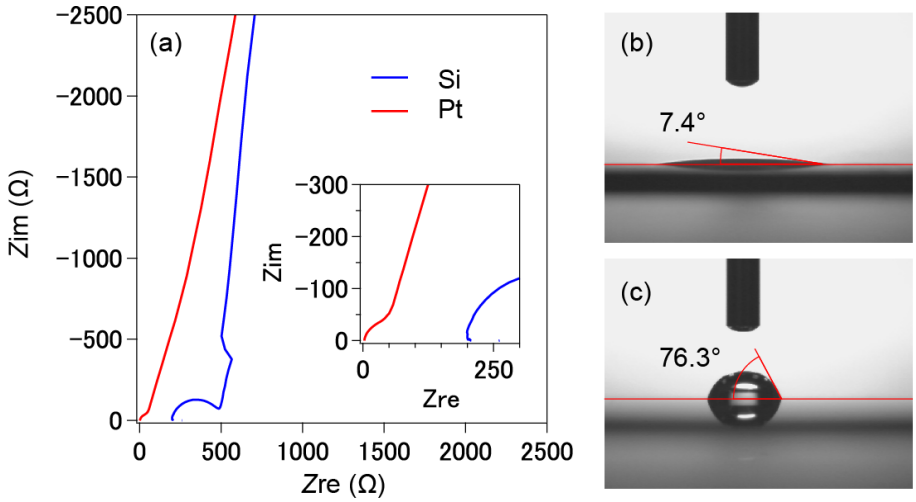

Figure 3. (a) Impedance plots of EDLCs consisting of Si and Pt electrodes. Side views of water droplet on (b) flat and (c) micro-porous Si electrodes.

From studies above, we learned that MEMS can fabricate high surface area Si electrodes with good wettability to electrolyte, but resistance need to be lowered by metal layer coating. These understandings motivated us to fabricate double micro-structured Si electrodes (DMSE) having miro-pillars covered by a micro-structured Au layer, which further increase surface area. Figure 4 shows (a) a plain view and (b) a cross-sectional view of Si rectangular micro-pillars of 100 μm depth and 15 μm width with a 10 μm gap in between. This pattern increases the surface area by 10.6 times than the flat

substrate. Figure 4(c) shows a cross-sectional scanning microscopic image of Au nano/micro-rods deposited on the micro-pillars. Morphology of the nano/micro-rods changes along depth of the micro-pillars because of shadowing effect during Au deposition. As show in the inset, near substrate surface, the micro-rods with a diameter of several micrometers densely cover whole area of the side wall, indicating large increase in the surface area. Each rod is apparently separated by air gap aligned parallel to the axis of the rods, which may provide preferable diffusion path for electrolytes of EDLC during charging/discharging.

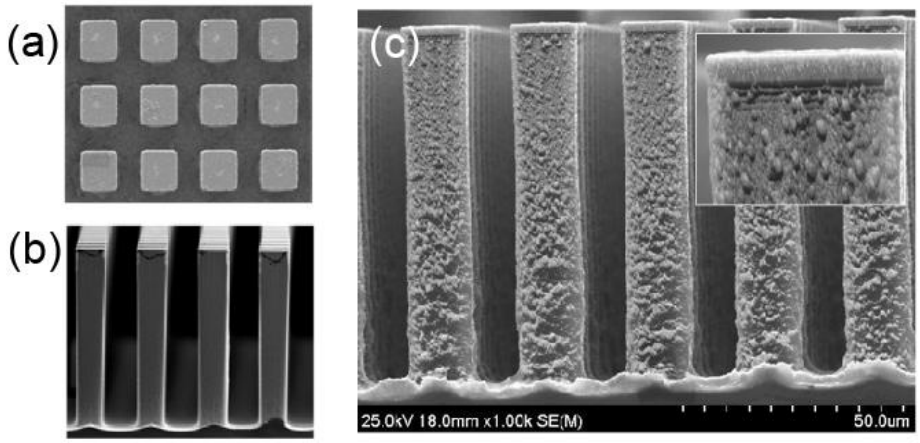

Figure 4: (a) Plain and (b) cross-sectional SEM views of silicon micro-pillars. (c) A cross-sectional SEM image of Au nano/micro-rods deposited on the micro-pillars.

Finally we implemented charge-discharge measurements by constructing EDLCs consisted of DMSE or Au electrodes. The $BMIMPF_6$ was used as an electrolyte. EDLCs were charged for more than 1 h by applying 1 V between electrodes, and then electrode potential was observed during discharging by flowing current of 0.1 μA. Fig. 5 shows discharging curve. Potential dropped rapidly for flat Au electrodes but very slowly (for more than 2 h) for the DMSE, clearly indicates significant increase in the capacity for the latter due to increased surface area. Actually calculated capacitance for DMSE is 14.3 mF/cm_2, which is about 530 times larger than that for flat Au.

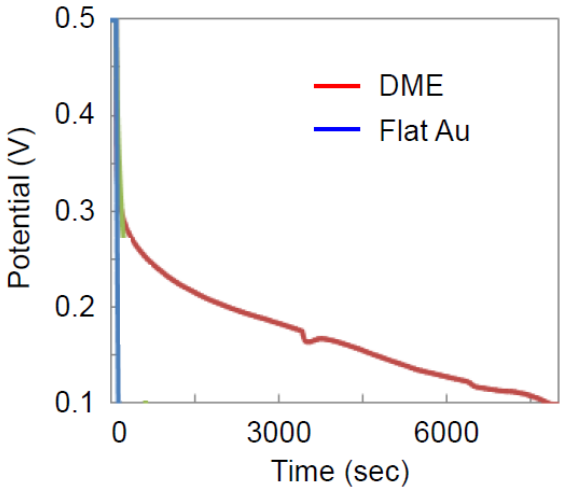

Figure 5: Discharging curves of EDLCs with DME and flat Au as electrodes.

4. Conclusion

This study challenged to make basis for the Si electrodes for EDLCs. We successfully demonstrated that MEMS processes can fabricate micro-structured high surface area Si electrodes. Furthermore we revealed that the micro-structured Si electrodes benefit from high wettability to the electrolytes, and electric resistivity can be lowered by surface metal coating. Based on these understandings, we fabricated the double micro-structured Si electrodes with micro-pillars covered by Au nano/micro-rods. The EDLC consisting of this electrode showed capacity of 14.3 mF/cm_2, which is about 530 times larger than that for flat Au. We believe that this study pave the way for Si-based EDLCs for the micro-sensor nodes.

References

[1] J. P. Norgaard, N. B. Lorentzen, R. Petersen and M. B. madson. *Growth of Nanostructures by Glancing Angle deposition (2007).*