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Short communication

Electrochemical properties of silicon deposited on patterned wafer

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Abstract

An amorphous silicon thin-film deposited on a patterned wafer is prepared by radio-frequency (rf) magnetron sputtering and is characterized by X-ray diffraction, galvanostatic cycle testing and field emission scanning electron microscopy. The specimen is assembled in cell of configuration: silicon working electrode/1 M $LiPF_6$ in EC/DMC, electrolyte/lithium metal, counter electrode (EC = ethylenecarbonate; DMC = dimethyl carbonate). A patterned silicon (1 0 0) wafer prepared by photolithography and KOH etching is used as the electrode substrate. The size of the patterns, which are composed of arrays of the negative square pyramids, is 5 μm/side.

The patterned specimen (silicon film on patterned substrate) is compared with a normal specimen (silicon deposited on a flat substrate). The rate of capacity fade on cycling is monitored as a function of the voltage window and current density. The patterned specimen displays better cycle behaviour at a high current density (high *C*-rate).

During the cycle tests at 200 μA cm^{-2}, the silicon electrodes yield an initial capacity of 327 μAh (cm^2 μm)$^{-1}$. After 100 cycles, the capacity is 285 μAh (cm^2 μm)$^{-1}$ and the capacity retention is 86%. Capacity retention is 76 and 61% at cycles 200 and 300, respectively.
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Keywords: Silicon; Patterned wafer; Thin film; Anode; Lithium-ion rechargeable batteries; Capacity retention cycle tests

1. Introduction

There is a growing demand for high specific-energy density, long-life, compact power sources for small portable electronic devices. In order to develop such power sources, research on thin-film, rechargeable lithium batteries has been intensified. Research on such batteries is being conducted in two major areas: (i) the development of optimized materials; (ii) improved electrode structures.

The anodes (negative electrodes) in most commercial lithium-ion batteries are composed of carbon-based materials. The reversible capacity of carbon-based materials is, however, limited to 372 mAh g^{-1}. In order to increase the specific energy, tin and silicon-based compounds have been examined as possible anode material alternatives [1].

Silicon is recognized as an active material with a potentially high specific energy for lithium battery applications. For example, $Li_{22}Si_5$ has a theoretical capacity of 4200 mAh g^{-1} [2]. This alloy material is made by Li insertion and extraction (volume expansion ratio: 4.12). The insertion of a large amount of lithium is accompanied by severe volume changes in the host material. The insertion induces mechanical strains that cause the electrode to crack, and, eventually to disintegrate and fail after a few cycles [3]. Thus, capacity fading on cycling is rapid. Many attempts have been made to improve the electrochemical performance and minimize the mechanical stress caused by the large volume change of Si-based alloy electrodes. The research has focused on reducing the particle size of the host material by using multi-phase materials or intermetallic compounds [4]. Nevertheless, such approaches do little to improve irreversible capacity loss and low cycleability [2]. Since we are interested in finding a way to make a thin-film Li-rechargeable battery integrated on to a

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Si chip, it is necessary to find a solution to the above materials problem.

Thin-film electrodes prepared by vacuum technology have good cycleability, but life is limited at high charge–discharge rates. This is due to an increasing surface concentration of adsorbed Li on alloying and difficulties on accessing all the lithium in the ZPC (zintl phase compounds) on de-alloying, at high current density conditions [5]. Limited cycle performance may also result from an increase in the ohmic (IR) drop due to the high current density and an overpotential related to lithium diffusion kinetics [6].

An effective way to improve the cycling stability of metal-alloy electrodes is to modify their morphology by reducing their particle size to few nanometers, or by designing special nano-structures [3]. Our approach to enhance the high-rate properties is to change the electrode structure by using a patterning process. Several other researchers have studied the effect of electrode structure on battery performance. Green et al. [5] have suggested that a nano-structured pillar surface can be formed on Si electrodes Li et al. [7] formed nano-fibrils using a specific template technique. Kushida et al. [6] fabricated of the order of hundred microns in size by using dry etching. They showed that electrode structure may play an important role in the development of lithium batteries. With suitable morphology modifications, electrode and electrolyte materials, which are considered still to be inadequate, may become crucial components of future innovative and powerful cell structures [6]. Chamran et al. suggested the use of an electrode produced from deep reactive-ion-etched Si templates [8].

This paper investigates the charge–discharge characteristics of a thin-film silicon electrode on a patterned substrate in an attempt to overcome the problem of mechanical disintegration due to volume changes during Li insertion/removal. Expanding the contact area between the deposited film and substrate should help the active Si material to accommodate volume change without disintegration. In order to induce regular cracking during cycling, micro-patterned, thin-film batteries have been fabricated by means of photolithography. This technology is commonly employed in micro electro-mechanical system (MEMS) processes. A patterning process is used for the substrate Si wafer. In order to form the new substrate structure, conventional lithography and etching techniques are adopted.

2. Experimental

The experimental process was comprised of the following steps: patterning process of substrate, thin film deposition, cell fabrication, cell testing, and film analysis. The patterning process and deposition sequence are shown in Fig. 1. The characteristics of the patterned specimen and a normal specimen were compared. The patterned specimen was an electrode consisting of silicon/copper deposited on a patterned wafer, while the normal specimen was an electrode consisting of silicon/copper deposited on an un-patterned wafer.

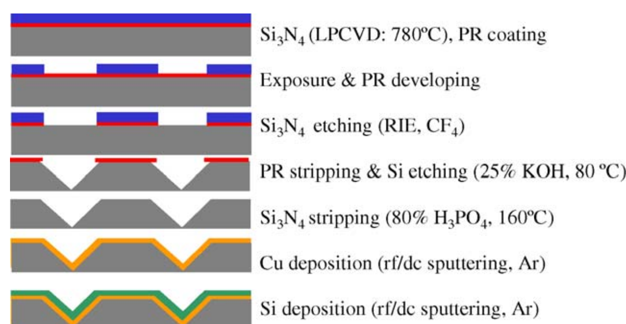

Fig. 1. Substrate processing and deposition procedure.

2.1. Patterning process of substrate

The Si(1 0 0) wafers were patterned as follows: wafer cleaning, silicon nitride deposition as a mask, photolithography (photoresist spinning, exposure, and development steps), silicon etching, removal of the silicon nitride. An optical Cr-mask patterned with a 5 μm-diameter-dot array (10 μm pitch) was employed.

2.1.1. Cleaning

A $H_2SO_4/H_2O_2 = 4/l$ (v/v) solution was used to remove organic impurities and particles from the wafer surface. Next, natural oxides and metal impurities were removed with hydrofluoric acid solution (10:1 HF, v:v) for 10 s. Finally, the wafers were rinsed with deionized water.

2.1.2. Silicon nitride chemical vapour deposition

A SiN_x film was prepared by low-pressure chemical vapour deposition (LPCVD). The SiN_x films with a thickness of about 200 nm were deposited on single crystalline Si(1 0 0) wafers. The process was performed at a temperature of 780 °C and a pressure of 40.75 Pa. Dichlorosilane ($Si_2H_2Cl_2$) and ammonia (NH_3) were used as silicon- and nitrogen-containing precursor gases, respectively. Prior to film deposition, the loaded reaction furnace was evacuated to a base pressure of 20 mTorr using a $Si_2H_2Cl_2$ flow rate of 30 standard cubic centimeters per minute (sccm) and a NH_3 flow rate of 100 sccm.

2.1.3. Photo-lithography

The negative photo-resist was spin-coated on silicon substrates at 500 rpm for 10 s and 3000 rpm for 30 s, consecutively. After spin coating, the films were soft baked at 100 °C to evaporate the solvent and to improve adhesion to the substrate. For the generation of patterns, the films were selectively irradiated by a mercury lamp (“Karl-suss”, MA-6). The exposed films were developed in an isopropyl alcohol bath and then post-baked at 110 °C.

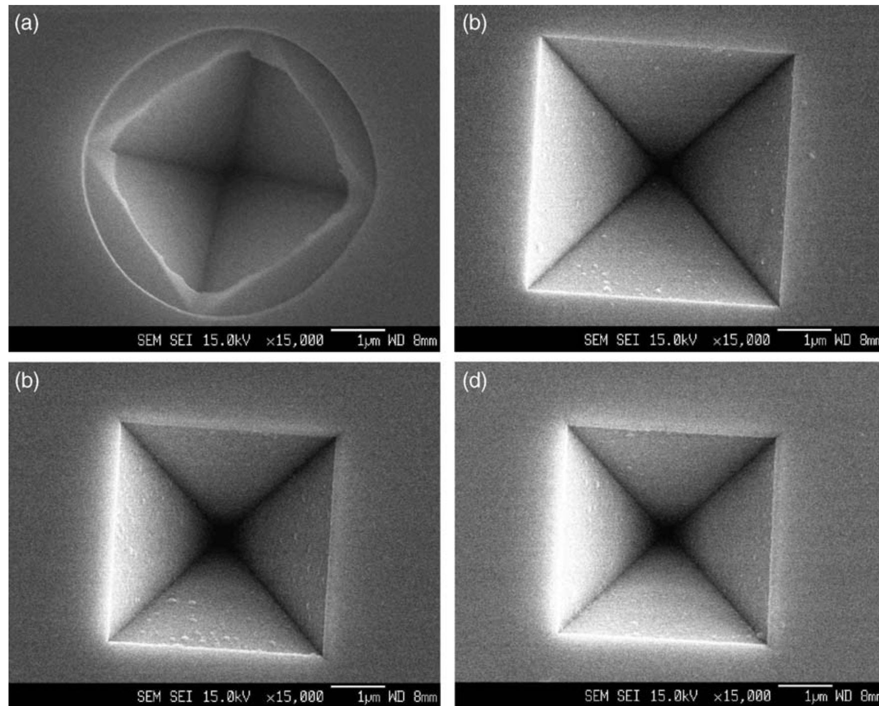

Fig. 2. Electron micrographs of (a) patterned Si wafer, (b) after Si_3N_4 striping, (c) after Cu deposition and (d) after Si deposition.

2.1.4. Silicon nitride reactive ion etching (RIE)

A RIE pattern transfer was performed using a dry-etcher (P-5000, Applied Material Korea). The parameters used to control the etch characteristics included the input gas and flow rate (CF_4, 5 sccm: CHF_4, 25 sccm: Ar, 70 sccm), power (60 W), chamber pressure (17.33 Pa), temperature, etching time, and passivation.

2.1.5. Si-etching

Formation of the electrode structure on the Si(1 0 0) wafer by means of anisotropic etching results from the interdependences of the (1 0 0) plane etching rates and the basic high-indexed planes. The shapes obtained under anisotropic etching were compared with the etching rate values of various crystallographic planes [9].

Patterns which shaped the negative regular square pyramids are arrayed with a 10 μm pitch. The pattern shapes are shown in Fig. 2 (plane view) and Fig. 3 (cross-section view). The patterns were developed with wet solution and formed by anisotropic 25% KOH etching at 80 °C. The etching rate of the Si(1 0 0) was 0.7 $\mu m\,min^{-1}$. The patterns were etched at a depth of 3.5 μm on the Si(1 0 0) for 7 min.

2.1.6. Silicon nitride strip

Silicon nitride used for masking during KOH etching was stripped with 80% H_3PO_4 at 160 °C.

2.2. Deposition of anode materials

Copper and silicon thin films were deposited by radio-frequency (rf) magnetron sputtering. The chamber was evacuated down to 4.07×10^{-4} Pa as a base pressure and a working pressure of 6.78×10^{-1} Pa was maintained with Ar gas. First, with a constant power density of $1.5\,W\,cm^{-2}$, 100 nm thick Cu films as a current collector were deposited on patterned wafer specimens. Then, Si films as anode material were deposited on the copper-coated substrates.

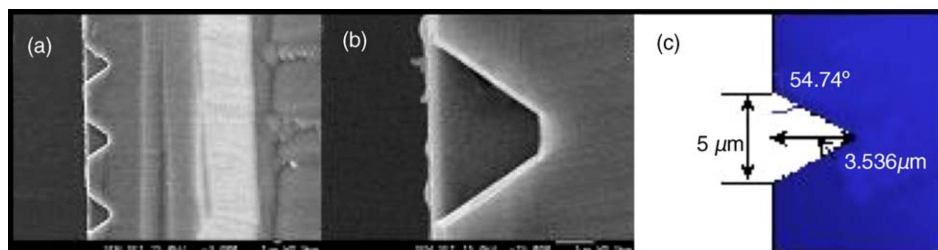

Fig. 3. Electron micrographs of cross-section: (a) 3000×; (b) 15,000×; (c) schematic figure of pattern shape.

2.3. Fabrication and testing of cell

Electrochemical measurements were conducted with a typical beaker-type cell. The cell was composed of the Si film as a working electrode, a metal lithium foil as a counter electrode, and a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M $LiPF_6$ as electrolyte. The cells were assembled in an argon-filled dry box. Galvanostatic charge–discharge measurements were performed with a cycle tester (WBCS 3000, WON A TECH). Static current tests were conducted at a constant current density of 160, 200, 240, 280 A cm^{-2} and charge–discharge tests at current densities of 120–160–200–240 $\mu A\,cm^{-2}$. The cell was cycled between the initial open-circuit voltage (OCV) and 0.08 V versus Li^+/Li, then between 0.08 and 1.0 V after the first cycle.

2.4. Characterization of specimen

The crystallinity of the samples was characterized by X-ray diffraction (XRD, RINT 2000, RIGAKU). The surface morphology of the films was examined by means of field emission scanning electron microscopy (JES 6340F, JEOL). The film thickness was measured by the profilometric method (Alpha-Step 500, TENCOR).

3. Results and discussion

3.1. Characterization of silicon thin film

The thickness of the silicon layer for the electrochemical test was 130 nm and that of the copper layer was 100 nm. The crystallinity of the thin film of Si deposited on the wafer was examined by XRD. Diffraction peaks, except those of Cu (JCPDS 03-1005) as the current-collector, could not be detected in the XRD patterns. In general, the production of amorphous material is well suited to thin-film techniques such as rf sputtering or evaporation. The amorphous, structure of the electrode is usually more open than that of a well-crystallized counterpart. It has been recognized that an open structure will adequately prevent lattice expansion and has many lithium diffusion paths [4,10].

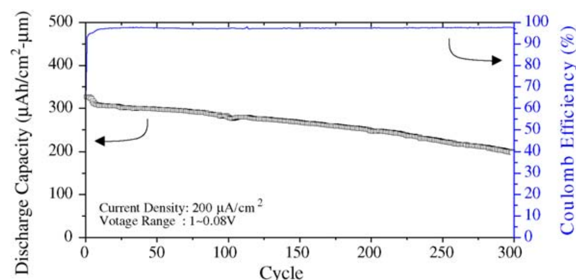

Fig. 4. Cycle performance of patterned specimen (Si/Cu films deposited on patterned wafer). Test conditions: current density 200 $\mu A\,cm^{-2}$; voltage range 1–0.08 V.

3.2. Electrochemical characterization of patterned specimens

The electrochemical discharge capacity and coulombic efficiency are presented in Fig. 4. To perform the cell tests a thin Si film of 130 nm thickness was deposited on to the substrate (Cu film on patterned wafer) at a current density of 200 $\mu A\,cm^{-2}$ and a voltage window of 1–0.08 V. The initial discharge volumetric capacity of deposited film was about 331 $\mu Ah\,(cm^2\,\mu m)^{-1}$. Capacity retention was 86% (285 $\mu Ah\,(cm^2\,\mu m)^{-1}$) at 100 cycles, 76% (254 $\mu Ah\,(cm^2\,\mu m)^{-1}$) at 200 cycles, and 61% (200 $\mu Ah\,(cm^2\,\mu m)^{-1}$) at 300 cycles. The capacity is defined as the total charge inserted into the projected electrode surface area exposed to the electrolyte (ignoring any surface area due to structuring), and is reported as $\mu Ah\,cm^{-2}$

3.3. Comparison of patterned specimen and normal specimens

The behaviour of the patterned and normal specimens were compared at high-current rates. It was expected that the adhesion and capacity retention of active film would be higher on patterned substrate.

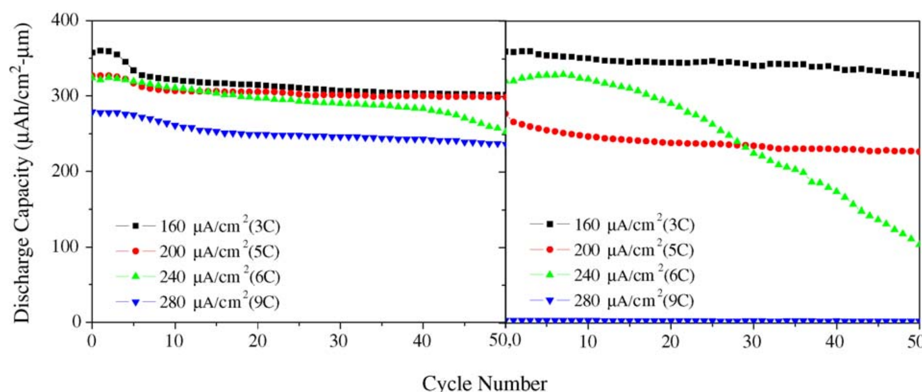

Fig. 5. Cycle performance of: (a) patterned specimen: Si/Cu films deposited on patterned wafer; (b) normal specimen: Si/Cu films deposited on normal wafer.

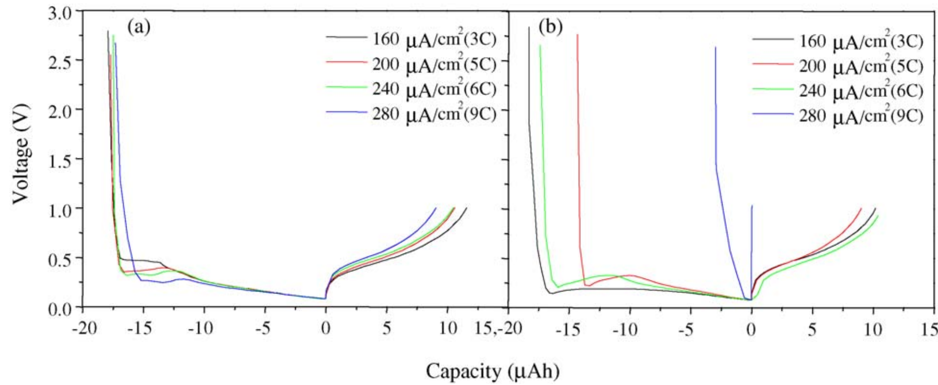

Fig. 6. Voltage profile of 1st cycle: (a) patterned specimen: Si/Cu films deposited on patterned wafer; (b) normal specimen: Si/Cu films deposited on normal wafer.

The cycle performance and voltage profile are shown in Figs. 5 and 6, respectively. Static current tests were performed at 160, 200, 240 and 280 μA cm^{-2}. At higher current densities, a Si film on the un-patterned wafer has a lower capacity and cycleability. In our experience, 280 μA cm^{-2} is the limiting current density condition for a 130 nm Si film. The cycle performance of patterned and normal specimens is given in Fig. 5. At a current density of 160 μA cm^{-2}, the difference in the cycleability of the two specimens does not appear to be large. At higher current densities from 200 to 280 μA cm^{-2}, however, the normal specimen shows a drastic decline in capacity down to 10 cycles at 240 μA cm^{-2}. It does not exhibit any capacity at 280 μA cm^{-2}. On the other hand, the capacity of the patterned specimen remains at 50 cycles at high current density of 280 μA cm^{-2}. The voltage profile of the first cycle of the patterned and normal specimens is presented in Fig. 6. The Si film on the patterned and flat wafers was tested between 0.08 and 1.0 V versus Li/Li^+ at various current densities. The voltage profiles of the patterned specimens are not affected by changes in current density. By contrast, the voltage profiles of the normal specimens are greatly influenced by changes in current density. The patterned specimens exhibit better cycle behaviour than the normal specimens at a high current density. The patterned specimen voltage profile shows a relatively small initial voltage, which implies that the patterned specimen has a small internal resistance.

The cycle performance of the patterned and normal specimens at 240 μA cm^{-2} is given in Fig. 7. Capacity retention at 40 cycles for the patterned specimen and normal specimens is 88 and 56%, respectively.

To evaluate cycle performance at various current densities the latter were increased from 120 to 240 μA cm^{-2} at 40 μA cm^{-2} increasing intervals every 10 cycles. The patterned specimen is found to have better cycleability than the normal specimen at high current density conditions, see Fig. 8. Scanning electron micrographs of both specimens after current density change test are presented in Fig. 9. The micrographs show that the normal specimen suffers loss of the active material (Si film) whereas the film of the patterned specimen remains dense and smooth. These images show that an amorphous Si film on the patterned substrate has a larger adhesion force.

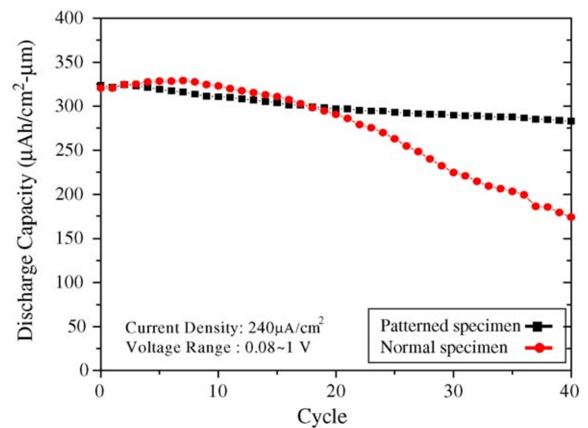

Fig. 7. Cycle performance comparison of patterned specimen and normal specimen at test conditions of current density 240 μA cm^{-2}, voltage range 1–0.08 V.

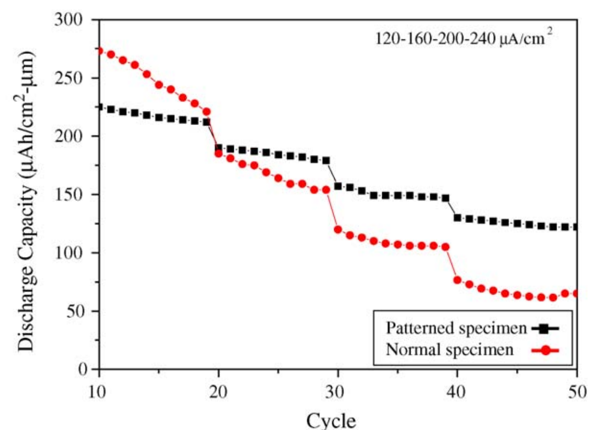

Fig. 8. Capacity retention property comparison of patterned specimen and normal specimen at current density change test (120–160–200–240 μA cm^{-2}).

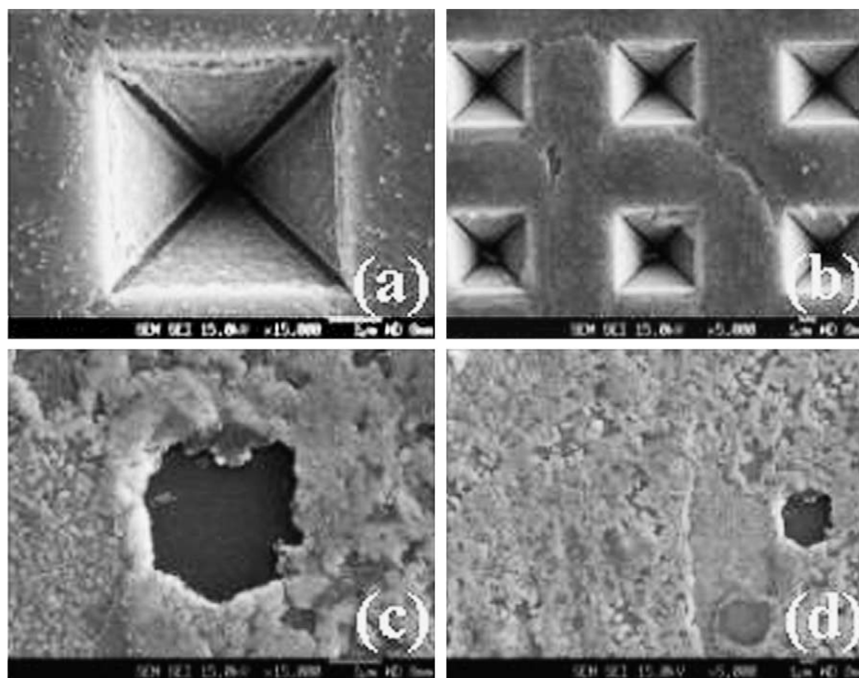

Fig. 9. Electron micrographs after cycle test (120–160–200–240 $\mu A\,cm^{-2}$): (a, b) patterned specimen; (c, d) normal specimen; (a) 15,000×, (b) 5000×, (c) 15,000× and (d) 5000×.

3.4. Effect of substrate patterning

The contact area between the Si and Cu films and the Cu film and the wafer, was increased by wafer (substrate) patterning. In general, an increase in the contact area improves adhesion. Through such an effect the active Si material can withstand volume change at high current density and capacity retention is improved. Electron micrographs (Fig. 9) after cycle testing reveal the influence of the shape of the patterned specimen on cell properties. Because of stress concentration at the etched edge, a crack is generated from the patterning edge and grows uniformly throughout the patterning shape. This phenomenon is called the shape effect of patterns. Briefly, the specimen shape effect refers to stress relaxation due to an induced regular crack. The crack is caused by surface stabilization after cycle testing.

4. Conclusions

Electrode structure is changed using a patterning process in order to improve the cycle performance and the capacity retention properties of an active Si film at high current rates. A thin Si film on a patterned substrate displays improved cycleability compared with an untreated flat substrate. A patterned specimen of 130 nm thick silicon exhibits good capacity retention at 200 $\mu A\,cm^{-2}$, 86% at 100 cycles, 76% at 200 cycles, 61% at 300 cycles. It is concluded that expanding the contact area between the deposited film and substrate helps the active Si material to accommodate volume changes at high current rates. An induced regular crack in thin films is seen in electron micrographs. The induced regular crack affects the stress relaxation of the film, and this is referred to as a patterning effect.

Acknowledgement

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