ナノ構造エネルギー変換貯蔵デバイスの非平衡電気化学プロセシング

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Non-equilibrium Electrochemical Processing of Nano-structured Energy Conversion & Storage Devices

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Abstract: JAXA Nanomaterials WG has engaged in Electrochemical Processing of Nanostructured Semiconductor Devices in renewable energy field. ZnO Nanowire Formation Mechanism has been focused. Present interest also extends to Electrochemical Processing of Si Nanowire in Ionic Liquid and High Temperature Molten Salt. Amorphous SiO_2 powder refined from diatomaceous earth (5N in purity, DE-SiO_2) was electrolytically reduced to Si at 1.00 and 1.20V vs. Ca^{2+}/Ca in molten $CaCl_2$ at 1123K. Electrochemical processing of Si micro- or nano-rod is now challenged as well as Li electrodeposition in ionic liquids. Now that ESA team shares the similar academic interests, we have decided to reorganize our team. "Electrochemical Nucleation & Growth" ESA ITT (PI: Prof. M. Rosso) has just started the activity in 2010. The team covers 4 categories: 1) Electrochemical Nucleation and Growth, 2) Dendritic Growth Process, 3) Kinetic Monte Carlo Simulation and 4) Gas Evolution Electrode. In order to support ESA research team, electrochemical nucleation phenomena of metals are examined with micro- or even nano-capillary electrode fabricated by anodic oxidation process.

Key words; Direct electrolytic reduction, Amorphous SiO_2 powder, Diatomaceous earth, Molten salt electrolysis, Low-cost Si production, Si & Li electrodeposition, Ionic Liquid, ZnO nanowire

Research Background

JAXA Nanomaterials WG organized by Dr. K. Kinoshita has focused on the following two projects.

(1) Gravitational Effects on Electrochemical Processing of ZnO Nanowire Arrays

Free standing ZnO nanowire array was successfully electrodeposited on ITO/FTO substrate by template-free method in $Zn(NO_3)_2$-$LiNO_3$ aqueous solutions in two different electrode configurations of (C/A) and (A/C). PL characteristics are measured at randomly selected locations in the deposited array sample. The transient current variation process accompanied by potentiostatic electrodeposition was classified into 4 stages corresponding to (a) NO_3^- ion reduction, (b) Induction period, (c) ZnO nucleation and growth and (d) ZnO NW arrays growth period controlled by mass transport process. The electrodeposition process with cathode over anode configuration (quasi-microgravity condition) was compared with anode over cathode configuration. The gravitational strength effect was thus clearly observed not only in morphological variations but also in photo luminescence measurement. That is, the uniformity of PL within a sample was drastically improved and the peak intensity caused by oxygen vacancy was considerably restricted.

(2) Electrochemical Processing of Si Nanowire in Molten Salt and Ionic Liquid

A possible way to electrodeposit Si has been studied in trimethyl-n-hexylammonium bis (trifluoromethylsulfonyl) imide containing 0.1 mol L^{-1} $SiCl_4$. Cyclic voltammetry suggests that $SiCl_4$ should be reduced to form Si around −2.0V. Potentiostatic electrolysis at this potential forms a yellowish-brown film on a Ni substrate. X-ray photoelectron spectroscopy and Raman spectroscopy reveal that the electrodeposited film

contains amorphous Si. It is also found from SEM observation and EDS analysis that highly uniform and dense thin film can be obtained in the initial stage of electrodeposition and that the electrodeposited Si film becomes rougher and thicker with the progress of electrolysis. Moreover, nanoimprint lithography technique provides a way to fabricate Si NW arrays for higher efficiency PV application.

These two subjects suggest us how important to independently control nucleation and growth process in order to rationally fabricate nanostructured energy conversion and storage devices which performances require larger interfacial area. Moreover, they require to provide the technological fundamental background which guarantees for us to quantitatively understand the coupling phenomena between the mass transfer rate and the morphological or microstructural variations during phase transformation like solidification or electrodeposition. Electrochemical reaction frequently demonstrates the advantageous aspects because the reaction can be relatively easily controlled by potential or current. The mass or heat transfer rate is obviously influenced by the induction of natural convection. The gravitational level surely affects the coupling phenomena confined inside meso- or nano-scale space. That is, here is our motivation to study the gravitational level effect on the nonequilibrium electrochemical processing in the international space station as an extremely idealized experimental environment.

Generally speaking, it is not easy to recover the sample fabricated in the international space station in order to characterize the microstructure of deposited film even if the project would be conducted in space, but it is rather simple to only monitor the growth rate as transient variations of current with microelectronics circuit. Classical experiment of Ag electrocrystallization in a capillary tube was performed in early 1960 in Bulgaria by Budevski and Staikov. This technique must be the most promising subject for ESA-JAXA nucleation & growth research project. The present program is composed of the following items:

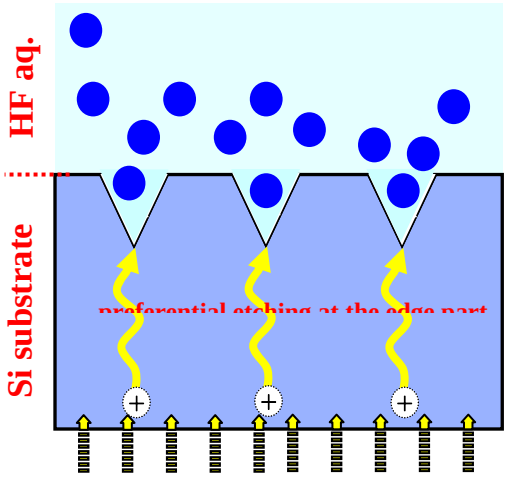
(1) Electrochemical Processing of Single Pipette with Micro to Nanometer Size Diameter
(2) Ag Nucleation Phenomena on FTO inside Single Pipette Reactor and FE-SEM Observation
(3) Measurement of pico-Ampere Transient Current Variation Accompanied with Nucleation
(4) SXS Technique
(5) Comparison between SXS and Transient Current Variation Wave
(6) Kinetic Monte Carlo Simulation
(7) Possibility to Grow Single Crystal NW?
(8) Transition of Dendrite Growth Mode and Simulation of Dendrite Growth Process

In this manuscript, the 1st matter is introduced in details.

Electrochemical Processing of Single Pipette with Micro to Nanometer Size Diameter

(a) High-Aspect-Ratio Pore Array

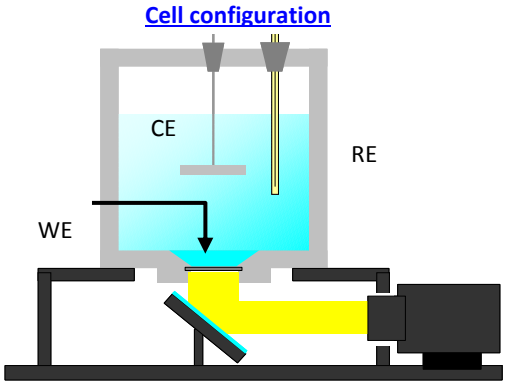
Figure 1 shows basic process steps to fabricate the array of high-aspect-ratio pores into Si wafer. N-type Si (100) wafers were used, whose front and back side surfaces were coated with 140nm thick Si_3N_4 layer by low-pressure chemical vapor deposition (LPCVD), which was then micro-patterned using photolithography and RIE. After dipping in 0.5wt% HF solution to remove the native oxide, the substrate was immersed in 20wt% KOH solution at 90 ℃ to form array of inverted-pyramid-shaped micropits at the surface by anisotropic etching. The micro-patterned Si_3N_4 layer serves as the protective mask for the alkaline etching, and the micropits act as initiation sites for the electrochemical etching to form high-aspect-ratio pores into the Si wafer. After the anisotropic etching, the entire Si_3N_4 layer on the back side surface was removed by RIE. Following this step, two types of patterned Au/Cr masks were formed on the back side surface. For the electrochemical etching process, the wafer was mounted at the bottom of an electrochemical cell and the back side surface of the wafer was illuminated using a halogen lamp (15V, 150W) during the etching to generate hole. In the case with the rim type Au/Cr mask entire back side surface was illuminated, while only selected areas, corresponds to the patterned areas of the front side surface were illuminated with the shade mask type one. Cross-sectional scanning electron microscope (SEM) images of the etched specimen demonstrated that the excess amount of the holes were supplied to the edge in the case with the rim type mask due to nonlinear diffusion of the holes, while such a nonlinear diffusion was inhibited with the shade mask type pattern aligned with the pattern pre-formed on the front side surface. Thus, the control of hole-diffusion condition is significant factor for the area-selective formation of the array of uniform pores into Si wafer. Another factor is how to control the mass transfer rate of hydrogen-associated Si fluorides such as SiH_2 (F_2) and SiH_2 (SiF).



$Si + 4HF_2^- + h^+ \rightarrow SiF_6^{2-} + 2HF + H_2 + e^-$

Si：band gap 1.11ev

（=1117 nm） ⇒ can be excited by halogen lamp



Electrolyte 1.0wt%HF+8.15wt%EtOH

Substrate: n(111)Si

Fig. 1 Principle of anode film oxidation process.

Silica tubes with tunable diameter (μm - nm order)

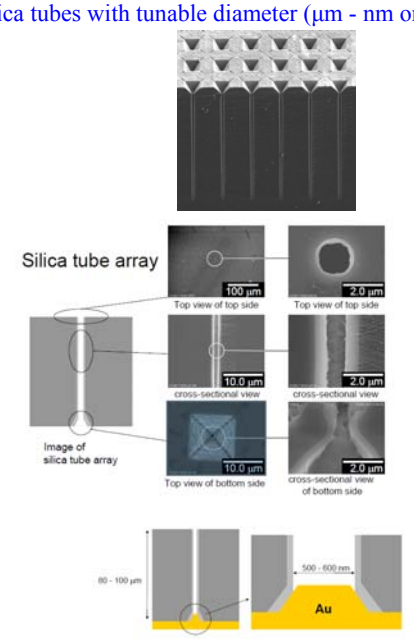


Fig. 2 On going project: T. Homma, Y. Fukunaka, T. Ouchi, O. Magnussen, R.C.Alkire