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Direct Writing of Si Nanostructures at Room Temperature by Electron Beam

Masahiro Mori[1], Masashi Akabori[1] and Takashi Masuda[1]

[1] JAIST
1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
Phone : +81-761-51-8603 E-mail : s1910212@jaist.ac.jp

Abstract

We demonstrate here the first electron-beam (EB) induced conversion from liquid Si (liq-Si), which is a precursor for semiconductor Si, to solid Si. Until now, liquid-to-solid Si conversion required 400 °C, however, the EB-induced conversion was progressed without any heating. Moreover, by introducing liquid phase electron beam induced deposition (LP-EBID) method, direct writing of Si nanopatterns were realized.

1. Introduction

Si is the most important material for semiconductor. Si industry has been developed using solid Si (wafer) and gaseous Si (silane) as starting materials. Recently, a precursor solution for semiconductor Si, called liquid Si (liq-Si) was reported.[1] Liq-Si provided attractive Si processing technologies based on liq-Si engineering (i.e. coating and printing Si [2-4]), which is not available to solid or gaseous Si. However, the critical disadvantage of the requirement of high processing temperature (400°C) for the liquid-to-solid Si conversion has prevented further development of liq-Si engineering.

Liq-Si is silicon hydrides and converted to semiconducting Si via the cleavage of Si-H (dehydrogenation) and recombination of Si-Si, which requires 400°C. In this study, we use electron beam (EB) irradiation to induce liquid-to-solid Si conversion, not using heat treatment. We also propose liquid-phase electron beam-induced deposition (LP-EBID) using liq-Si as a precursor material, instead of the conventional EBID which uses gaseous precursor materials. EBID irradiates a precise dose of EB in a quick and reproducible manner to a predetermined location under computer control, inducing localized dissociation and deposition of precursors. Therefore, LP-EBID of liq-Si would be a Si nano-patterning technology that does not rely on traditional photolithography. The purpose of this study is to demonstrate the potential of LP-EBID of liq-Si to fabricate Si nanopatterns without heating.

2. Experimental Details

As liq-Si, CPS (Si_5H_{10}) was synthesized according to the previous study. CPS was encapsulated in a liquid cell equipped with a SiN window (membrane) for EB (Figure 1). The cell was then introduced in an electron beam lithography system (ELIONIX ELS-3700) and irradiated with the acceleration voltage of 30 kV. The dose D (pC) is defined as [irradiation time (sec/shot), T] × [beam current (A), I] × [shot number, N]. The beam diameter was estimated to be 50 nm. After irradiation, the SiN membrane was removed from the cell and the surface in contact with liq-Si was observed by scanning electron microscope (SEM).

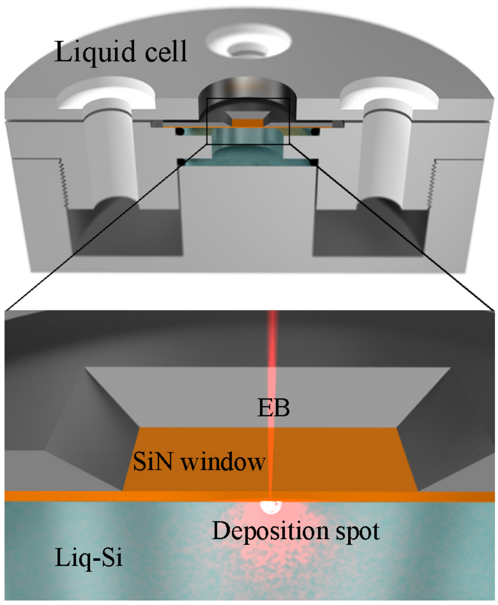
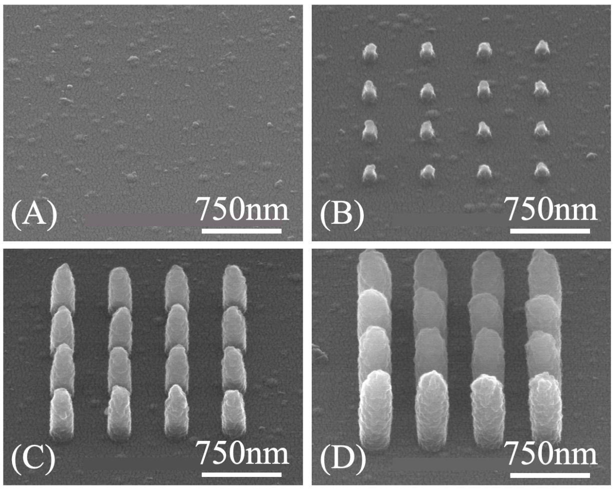


Figure 1. Liquid-phase electron beam induced deposition (LP-EBID) of liq-Si. The schematics of liquid cell and EB irradiation.

3. Results and Discussion

The 4×4 array of single-pixel dots were deposited by changing the dose (1.6–20 pC), as shown in Figure 2. The irradiation parameters are also listed in the figure. Deposits with diameters of 100 to 200 nm were observed at the dose above 4.0 pC, and the sizes increase with dose. Threshold dose was around 1.6 pC. Figure 2 indicates that size-controllable nanopatterns are obtained by changing the dose.

To measure phonon band of the deposits, larger deposit was prepared by giving sufficient doses until the deposit growth was saturated. Figure 3(a) shows an SEM image of resultant deposit with a height and a diameter of several micrometers, and Figure 3(b) represent the Raman spectrum of the deposits. This spectrum corresponds to that of typical amorphous Si (a-Si), indicating that the EB irradiation induces the liquid-to-solid Si conversion. Cross-sectional transmission electron microscope combined with energy dispersive X-ray spectroscopy (TEM-EDX) analysis revealed that the deposit was pure Si (not shown here).



The irradiation parameters

	I [pA]	T [μs/shot]	N [times]	D [pC]
(A)	200	500	16	**1.6**
(B)	200	500	40	**4.0**
(C)	200	500	100	**10**
(D)	200	500	200	**20**

Figure 2. Scanning electron micrographs of obtained Si arrays (4 × 4 dots) with different doses from 1.6 to 20 pC and the list of irradiation parameters.

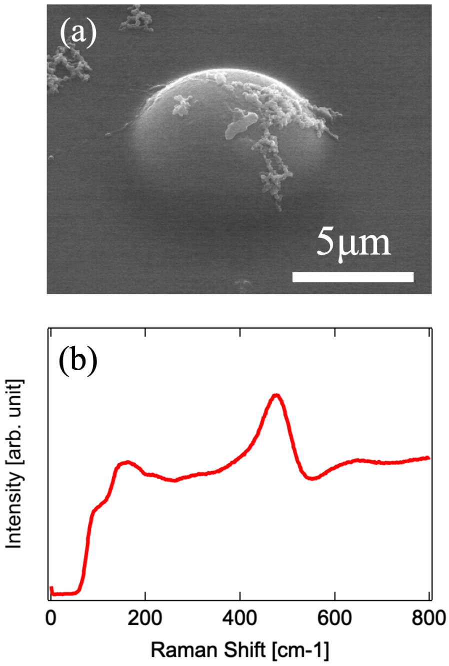


Figure 3. The deposit obtained by giving sufficient doses. (a) Scanning electron micrograph of bird's eye view (b) Raman spectrum.

4. Conclusions

This is the first attempt that EB-induced liquid-to-solid Si conversion. By LP-EBID of liq-Si, Si deposits with diameters of 100 to 200 nm were obtained without heating. Because Liq-Si is an ideal Si precursor solution consisting only of Si and H, the contamination-free deposition was realized, as opposed to conventional EBID which suffered from carbon contamination up to 90% [5,6]. LP-EBID of liq-Si realized direct writing of semiconducting Si which does not require heating and conventional photolithography processes. This resolution is an order of magnitude larger than the resolution limit of resist-based photolithography used in cutting-edge Si processing. The EBID system with higher acceleration voltages (smaller beam diameters) would be effective for obtaining higher resolution. Indeed, the resolution of 1 nm or less has been reported using conventional EBID with higher acceleration voltage [7,8]. Therefore, it is expected that LP-EBID of liq-Si would attain a processing resolution of approximately 1 nm or less using higher acceleration voltage. This technology would be a powerful tool for next-generation nano fabrication such as Si quantum dot, nano-optica patterns, 3D devices, mask repairing technologies.

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