Direct imprinting of liquid silicon

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ABSTRACT

A polymeric precursor solution for semiconducting silicon named “liquid silicon” was synthesized. The liquid silicon could be doped either n- or p-type by dissolving appropriate amounts of white phosphorus or decaboran, respectively, in the solution. Liquid silicon was spin-coated on substrates and was imprinted to obtaine fine patterns. Then the liquid silicon patterns were converted to amorphous or polycrystalline silicon at 400–700°C or above 800°C, respectively. Although a significant volume shrinkage based on the liquid-to-solid silicon conversion was observed, the well-defined angular patterns as well as electrical properties were obtained after imprinting. The direct imprinting of liquid silicon is expected to be used as microfabrication technology in the field of solution-based silicon devices

Keywords: liquid silicon, printed electronics, solution process, semiconductor, polymer

1 INTRODUCTION

Recent advances in frexible devices have principally supported by the progress of functional materials and patterning technique. In particular, solution-based semiconducting materials and printing technology are very important in the development of next-generation frexible electronics. Recently, low-cost microfabrication technique using solution-based materials, like microcontact [1], ink-jet [2], and nanoimprint [3], have been studied well. In particular, nanoimprint, which was initially proposed by Chou et al [4], has an attension because of its potential to replace conventional photolithography in patterning process. Direct imprinting using a wide vaiety of functional materials such as polymer resist, sol-gel materials, nanoparticle-based dispersion have been under intense study.

In this study, we syntheiszed a polymeric precursor solution for semiconducting silicon named “liquid silicon”, and imprinted it to obtaine well-defined and fine patterns directly. The imprinted patternes with the dimensions of several hundreds of nanometers or less were then converted to semionducting silicon via thermal decomposition. The technique developed in this study is expected to become a microfabrication method for the cutting-edge silicon patterning, which are indispensable to realize printed silicon electronics.

2 EXPERIMENT

“Liquid silicon” was synthesized, as show in Figure 1. Either p-type or n-type liquid silicon was also synthesized by dissolving appropriate amounts of white phosphorus or decaborane, respectively, in the solution [5]. The liquid silicon is converted to bulk silicon via dehydrogenation.

Polydihydrosilane was synthesized by a photo-induced ring-opening polymerization of cyclopentasilane (Si5H10 [6–8]). The polydihydrosilane dissolved in cyclooctane at the concentration of 10–20 wt.% was spin-coated on a substrate at 2000 rpm for 30s. The resultant film was converted to solid silicon by heating at 100–800°C for 10 min under nitrogen atmosphere.

The approach to fabricate silicon patterns using nanoimprinting included the following steps (Figure 2): (a) the liquid silicon film was spin coated onto a substrate, and was cured at 160°C for 5 min on a hot stage; (b) a mold was pressed into the film at 10 MPa at 160°C for 10 min followed by 10 MPa at 200°C for 10 min to solidify the film; (c) the mold was released after cooling down to 160°C; and (d) the resultant patterned film was annealed at 400–800°C for 20 min to complete the conversion to solid silicon.

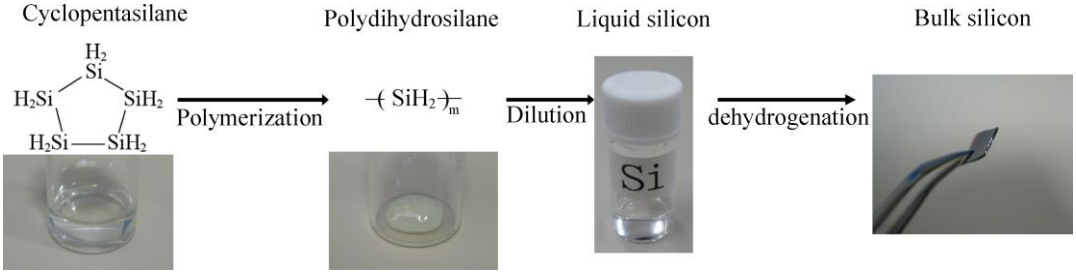

Figure 1: Preparation route for liquid silicon and solution-processed silicon.

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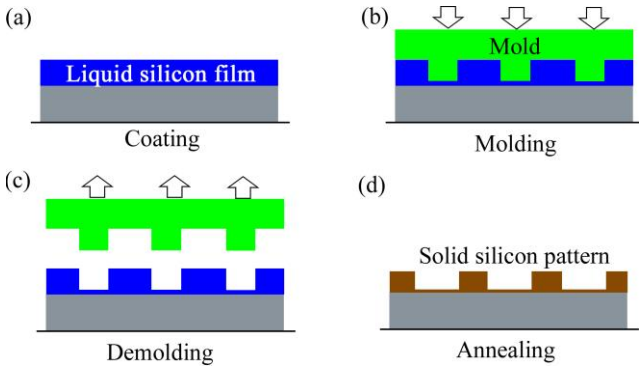

Figure 2: Imprint procedure of liquid silicon. (a) Liquid silicon was spin-coated on a substrate and cured at 160°C for 5 min. (b) A mold was pressed into the film at 10 MPa and at 160°C for 10 min, followed by the temperature was raised up to 200°C and kept it for 10 min with maintaining the pressure at 10 MPa. (c) The mold was released after cooling down below 160°C. (d) The resultant film was annealed at 400–800°C for 10 min to complete the liquid-to-solid conversion.

3 RESULTS AND DISCUSSION

3.1 Film properties

Liquid-to-solid conversion on liquid silicon was investigated. Figure 3(a) shows a photographic image of the solution-processed silicon films with a thickness of 80 nm and with various annealing temperatures. The films prepared below 270°C are transparence, and change from transparence to dark brown when the temperature is increased from 270 to 360°C. This change in color is attributed to a reduction of optical gap from that of polymer (6.5 eV [9]) to lower values.

The transparency of the films annealed below 270°C corresponds to an insulator material whereas the brown color of the films annealed above 300°C indicates an amorphous silicon. The cange in color at 800°C is attributed to crystallization, as supported by Figure 3(b), in which first-order Raman spectra of the films are shown. The typical phonon bands [10,11] of amorphous silicon at 470, 388, 302, and 150 cm^{-1} are observed in the films annealed at 360–700°C, whereas a sharp peak corresponding to crystalline silicon at 515 cm^{-1} [12] was observed in the film annealed at 800°C. These spectra are comparable with silicon films prepared using conventional vacuum-processing. Solution-processed amorphous and polycrystalline silicon films were obtained by heating at 360–700°C and 800°C, recpectively.

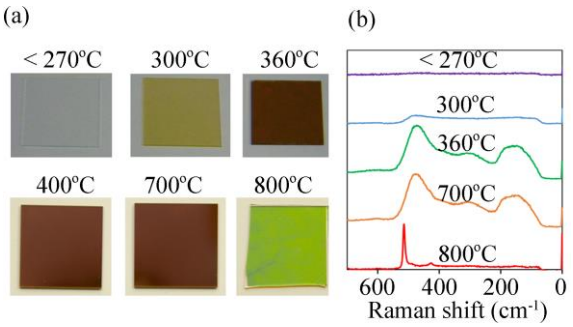

Figure 3: Solidification of liquid silicon film on a flat substrate. (a) Photographic image of solution-processed liquid silicon films with a thickness of 80 nm. The annealing temperature was from 270 to 800°C. (b) Raman spectra of the films. The spectra for the films with 400–700°C show amorphous silicon, whereas that for the film with 800°C shows polycrystalline silicon.

To study the liquid-to-solid conversion, thermal properties of polydihydrosilane was measured by thermogravimetry (TG) in Figure 4. TG and temperature/time derivation DTG signals are shown in red and black line, respectively. The TG data indicates a weight reduction of 58% by heating up to 360°C and consequentrly only 42% of the material remained in the form of amorphous silicon. The weight reduction is caused by desorption of hydrogen and hydrosilane compounds [13].

According to the DTG curves the major weight loss takes place at 100, 200, 300°C. The first peak at 100°C is attributed to the desorption of small-molecule hydrosilane [14]. The peak at 200°C likely represents the partial decomposition of the fragment in polydihydrosilane; namely, partial solidification of silicon in liquid silicon is occurred in this temperature range. This transitions are important considerations in the imprinting procedure. The peak at 300°C corresponds to the authentic decomposition of liquid silicon to form amorphous silicon [13]. The weight loss was very small at the temperature range above 360°C, indicating that the stable silicon was formed when the temperature exceeded that of the final consolidation peak.

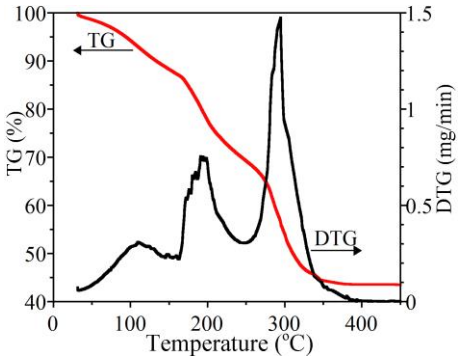

Figure 4: TG and DTG signals of polydihydrosilane as a function of heating temperature. Reproduced with permission from ref [13]. Copyright 2012 Elsevier B.V.

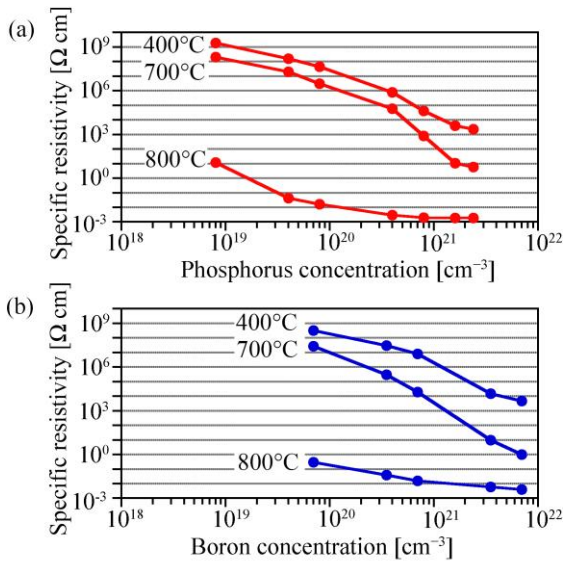

Figure 5: Specific resistivity of the doped silicon films with different annealing temperature and dopant concentration. (a) n-type silicon and (b) p-type silicon.

Figure 5 shows specific resistivity *R* as a function of dopant concentration in the film with 400 and 800°C. The dopant concentration was meaured by secondary ion mass spectrometry. Increasing the annealing temeprature lowered *R* because of dopant activation by heating. Nevertheless, the obtained *R* values for the coated film was an order of magnitude poorer than that for the conventional vacuum-processed film [15]. This poor *R* for the coated film would be due to defect density. The termination of dangling-bond defects with hydrogen reduced the *R* by one order of magnitude [5]. As compared to the amorphous silicon film, the *R* of the films with 800°C was decreased by three to seven orders of magnitude due to crystallization. As for non-doped amorphous silicon, photoconductivity under AM 1.5G with the intensity of 100 mW/cm^2 and dark conductivity were 1.1 × 10^5 Ωcm and 5.0 × 10^{10} Ωcm, respectively, which ic comparable value to device-grade vacuum-processed ones [16]. We concluded that the white phosphorus and decaborane can be used as an n-type and p-type dopant, respectively, in the liquid silicon.

3.2 Imprinting

Since an imprint makes replica of the relief pattern by mechanical embossing, the deformability of the polydihydrosilane film should be optimized for obtaining good patterns. Coated liquid silicon films were cured and imprinted around 100–200°C because the partial solidification of the film is induced in this temperature range, as mentioned above. The imprinted liquid silicon films were then annealed at 800°C to complete the liquid-to-solid conversion.

Figure 6 shows the scanning electron microscope (SEM) images of the mold and imprinted n-type silicon lines after

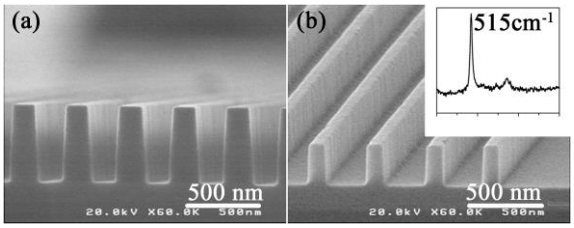

Figure 6: SEM images of (a) mold and (b) imprinted silicon lines after annealing at 800°C. Raman spectrum of the patterns are inserted in upper right.

	Mold	Imprinted silicon	Shrinkage ratio to the mold cavity (%)
Wider base (nm)	210	130	38
Nallower base (nm)	150	100	33
Height (nm)	520	270	48
Length (nm)	3× 10^6	3× 10^6	0
Volume (cm^3)	2.8× 10^{-10}	9.3× 10^{-11}	67

Table 1: Dimensions of a mold cavity, imprinted silicon line, and shrinkage ratio to a corresponding mold cavity. The sizes of each pattern were estimated from SEM images shown in Figure 6.

annealed at 800°C. A Raman spectrum of the silicon lines is inserted in upper right to confirm the phase, in which sharp peak corresponding to crystallin silicon was observed. Each dimension is summarized in Table 1. Although the volume reduction reached 67% (33% remained) after annealing at 800°C, well-defined angular patterns were preserved. Moreover, energy dispersive X-ray spectrometry revealed that both the oxygene and carbon contents in the imprinted area were less than 5 at.%, imdicating high-purity silicon [17].

Here we consider the volume shrinkage of liquid-to-solid conversion on liquid silicon. The TG analysis on polydihydrosilane in Figure 4 indicate a weight reduction from 160°C (imprinting temperature) to >360°C reaches 50%. Moreover, the density of the imprinted silicon at 160°C lies between 1 g/cm^3 (polymer) and 2.2 g/cm^3 (solid silicon [18]). Considering both the weight reduction and change in density, a volume shrinkage of 50–78% is expected during the conversion process. Obtained volume shrinkage of 67% is lies within the expected value.

The *R* of an isolated silicon line in Figure 6(b) was measured after etching of residual area between each line completely. The imprinted n-type polycrystalline silicon line with dopant of 8.1 × 10^{-20} cm^{-3} was 7 mΩcm, whereas the non-imprinted film was 2 mΩcm. Although the imprinted line was damaged slightly by the isolation process, the electrical properties showed acceptable values even after isolation.

4 CONCLUSIONS

In this work, we synthesized polymeric precursor solution for semiconducting silicon, named “liquid silicon”, and realized solution-processed amorphous/polycrystalline silicon by heating of liquid silicon. Moreover, we obtained well-defined fine silicon patterns by direct imprinting of liquid silicon.

Direct imprinting of liquid silicon is practical approach to realize silicon devices without photolithography process. The technique produced well-defined silicon patterns with high resolution and high throughput, demonstrating its potential for next generation silicon electronics in a field of nano-structured devices. The elimination of the conventional photolithography process in microfabrication of silicon devices is particularly important for realization of printed silicon electronics.

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