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Synthesis of Liquid-Silicon and its Inkjet Printing

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Abstract

Polymeric precursor solution for semiconducting Si called liquid Si (liq-Si) was synthesized. Moreover, the liq-Si was inkjet-printed and converted into amorphous or crystalline Si by annealing at 400 or to 1,000 °C, respectively. Satisfactory inkjet discharge properties and printed patterns were obtained using liq-Si consisting of polysilane with an average molecular weight of 2,500 g/mol. The resultant Si film had a flat surface with a root-mean-square roughness of 0.8 nm. These achievements were extended to n- and p-type Si films by synthesizing liq-Si chemically doped with white phosphorous and BH3-THF complex, respectively. Inkjet printing of liq-Si gives a well-defined Si pattern without using traditional photolithography processes, providing a possible means of realizing "printed Si electronics".

1. Introduction

Si is important material in semiconductor. Both solid Si (wafer) and gaseous Si (silane) have been employed as starting materials for Si devices. Recently, an attempt to fabricate Si devices using liquid-phase Si material (liq-Si) was reported [1]. A precursor for semiconducting Si, liq-Si consists of only Si and H (polyhydrosilane) and is converted into solid Si via dehydrogenation [2]. Liq-Si can extend the field of printed electronics, which have been limited to organic and oxide materials, to Si semiconductor industry.

The first report of liq-Si was the fabrication of poly-Si transistors using an inkjet method in 2006 by Shimoda et al [1]. They demonstrated the potential of liq-Si as a high-quality semiconducting Si, but also revealed the difficulty of obtaining a uniform and continuous film by inkjet printing. Since then, many solution-processed Si devises have been reported, but the liq-Si was spin-coated, blade-coated, or drop-casted because it is relatively easy to obtain uniform films using these methods [2-5].

Inkjet printing delivers a precise amount of liquid to a predetermined location quickly and reproducibly under computer control as a maskless patterning technique. Therefore, liq-Si inkjet printing become a Si patterning technology that does not rely on traditional photolithography. Unfortunately, this process has not been realized because of the unavailability of liq-Si for inkjet printing.

Herein, the potential versatility of liq-Si inkjet in the field of Si engineering by the direct patterning of intrinsic (i-type), p-type, and n-type Si films is demonstrated. In this study, three types of liq-Si (i-, p-, and n-type) for inkjet printing were synthesized and printed.

2. Experiment

Liq-Si is a polysilane $(SiH_2)_n$ solution. The polymer with the average molecular weight (Mw) of 2,500 g/mol was prepared according to the procedure described previously [6]. The p-type polysilane was obtained via the dehydrogenative condensation reaction between BH3 and Si–H. BH3–THF and i-type polysilane was mixed at [B]/[Si] = 0.02. The n-type polysilane was obtained via the co-polymerization of cyclopentasilane (CPS) with white phosphorus ([P]/[Si] = 0.01) at λ = 405 nm, 200 mW/cm^2, and 120 min. Each polysilane was diluted with cyclooctane solvent to a concentration of 5 wt%, and then vacuum degassed for 30 min. Inkjet printer PixDRO LP50 (SUSS Micro Tec) with inkjet head SL-128AA (Fujifilm) was employed. The droplet (65 pL) was printed in a periodic polka-dot pattern with a 70 μm pitch. The quartz substrate was kept at 50 °C during printing. Printed film was annealed at 400 °C (for amorphous-Si: a-Si) or 1,000 °C (for crystalline Si) for 20 min.

3. Results and discussions

Figure 1(a) and (b) shows a photograph of inkjet droplets in flight and printed film (after annealing at 400 °C), respectively. Droplets were stably discharged from all the nozzles. Furthermore, landed droplet formed well-defined patterns. Figure 1(c) shows a micrograph of the edge of the printed area. Although the edge of the printed area had some irregularities in film thickness and pattern, a uniform film (root mean square roughness = 0.8 nm) with a thickness of 40 nm was obtained inside the printed area. This irregularity is due to the non-uniform drying conditions. The landed droplets at the edge of the printing area are partially surrounded by other droplets, leading to anisotropic drying, which leads to a non-uniform film.

Figure 2 shows the Raman spectrum of the printed film. The phonon band spectra at 480, 390, 300, and 160 cm^{-1} were consistent with those of typical a-Si [7], indicating that the liq-Si was converted to a-Si by annealing.

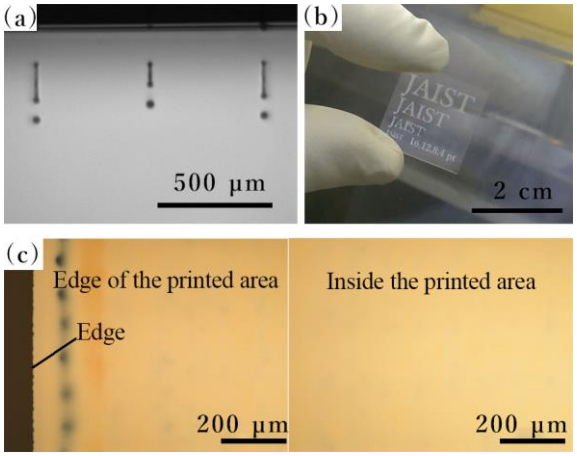

Fig. 1 Inkjet printing of liq-Si. (a) Inkjet droplets discharging from three nozzles. (b) printed Si pattern on substrate. (c) Micrographs of the printed area at edge and inside.

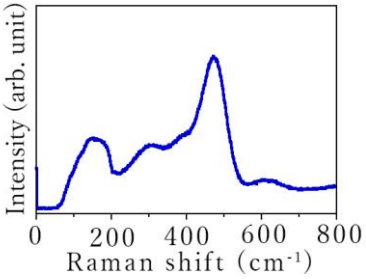

Fig. 2 Raman spectrum of printed Si film annealed at 400°C

The impurity concentrations in the Si film were quantified by SIMS, and listed in Table I, in which the density of Si is assumed to be 5×10^{22} cm^{-3}. The H of 8 at% was existed in the film, which is consistent with H < 10 at% observed in typical hydrogenated a-Si [8]. The C and O impurities are uptake from solvent and surrounding environment (natural oxidation). Although some impurities remain, the impurity concentration of the inkjet-printed Si film is equivalent to that of the spin-coated Si film [9]. We concluded that the inkjet process was not adversely affected.

Table I. Impurity concentrations in Si film

Element	Concentration (at%)
H	8
O	0.2
C	0.08

Doped Si films were also prepared using boron and phosphorous doped liq-Si. The electrical properties were listed in Table II. All Si films were crystallized by 1,000 °C to facilitate electrical property measurements. B and P doped liq-Si gave Si films with hall coefficients of 6.2 and –0.50 m^2/C, respectively, indicating each film works as p- and n-type. As for resistivity, i-type shows 7.7×10^6 Ωcm, whereas the p- and n-type films has 5.5×10^{-2} and 3.2×10^{-3} Ωcm, respectively. Chemically doped B and P in liq-Si would be incorporated into Si network and worked as dopants to control the electrical properties.

Table II. Hall coefficient and resistivity of crystalline Si films.

Dopant element	Hall coefficient (m^2/C)	Resistivity (Ωcm)
Non		7.7×10^6
B	6.2	5.5×10^{-2}
P	–0.50	3.2×10^{-3}

Although polysilane thermal decomposition has been used to obtain semiconducting Si, the doping process, chemical reaction, and underlying liquid-to-solid conversion processes have rarely been studied, and how each dopant is incorporated into the Si network during the annealing process remains unknown. We are currently calculating a reaction between dopants and Si–H bonds by density functional theory; if successful, such efforts could lead to effective doping.

4. Conclusions

We demonstrated the printing of liq-Si, which was then converted to an a-Si film by annealing at 400 °C. This was realized not only for i-type liq-Si, but also for n- and p-type liq-Si, which include phosphorus and boron, respectively. An important achievement of this work was the replacement of the Si patterning technology from a traditional subtractive method (photolithography) to an additive method (direct printing). We expect that the inks and technologies provided in this research will open up new avenues in printed Si electronics.

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