Thin-Film Solar Cell by Liquid Silicon

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Silicon(Si) is definitely one of the most important electronic materials. Until now, its solid and gas phases have been utilized as material sources while a liquid phase left almost unexplored. When the future sustainable industry is considered, however, a new process using liquid Si sources would be very attractive for the effective use of energy and material. As the first step of the practical use of liquid Si, we have developed a solar cell. Recently we succeeded to make a prototype and demonstrated its operation [1]. Here we will introduce four crucial points picked up among the various field ranging from raw material to device.

(1) Synthesis of a SiH polymer solution (liquid silicon) and analysis of its solution state

Cyclopentasilne(CPS)[2], which is a stable molecule (Si_5H_{10}) having a boiling temperature of 194 deg C, undergoes ring opening polymerization by UV light to become polydihydrosilane. We found a good solvent for polydihydrosilane so that polymerization process can be traced in terms of molecular weight change by SEC-MALLS system (SEC:size-exclusion chromatography, MALLS: multi-angle laser light Scattering) [3]. Fig.1 shows the polymerization process during irradiating the 365nm UV light with 1mW/cm2 up to 240 min. Synthesized polymer was diluted by an organic solvent to get a polymer solution or liquid To investigate its solution state, the relationship silicon. among three parameters, intrinsic viscosity [η], radius of gyration Rg and molecular weight, was deduced based on the scaling rule. It is found that polydihydrosilane tends to have a branched structure like nano particles[3].



Figure 1. Change of Molar mass distribution by SEC-MALLS for CPS and polydihydrosilane synthesized with irradiation time 30, 60 and 240 min dissolved in cyclohexene at 25 degree C.

(2) Coating liquid silicon on the substrate [4]

It was found that coating property of liquid silicon was totally governed by van der Waals interaction. To understand the coating phenomena, Hamaker constants of CPS, polydihydrosilane and solvents were measured by the SSM(simple spectral method) method[5]. Fig.2 shows the spin-coating result on the several substrates of which Hamaker constant are different each other. The liquid silicon used was a 1.5wt% polydihydrosilane solution in cyclooctan solvent. It clearly demonstrated that the larger Hamaker constant gave the better coating property, especially when the Hamaker constant is minus, the coated film broke during solvent drying to become a dot scattered structure.



Figure 2. Optical micrographs of polydihydrosilane films on different substrates. The A_{ALS} values calculated by the SSM are noted on each micrograph. The length of the bar in each image is 100 μ m.

(3) Transformation from polydihydrosilane to an amorphous Si (a-Si) film [6]

Different from an a-Si:H film from gas deposition, the film formation process using liquid silicon is a subsequence one from breaking of chains of polydihydrosilane, desorption of gases and formation of three dimensional Si-Si network. To grasp a picture view of the process, TG and DTA



Figure3. TG (bold solid line), DTA (thin solid line), and DTG (dashed line) curves of polydihydrosilane.

analyses were conducted in the glove box. Here we can see three characteristic peaks in Fig.3. Up to 360 degree C the weight reduction continues occurring to lead to an amount of weight loss of 58%. This loss was attributed to desorption of gas species such as SiH_x (x=2,3) and H₂ by TDS analysis[7]. In Fig.4 the films annealed at each temperature for 15 minutes are shown, indicating the distinct color changing at 300 degree C. Raman spectroscopy revealed the transformation from a polydihydrosilane film to an a-Si one at around 300 degree C. But the conversion to a semiconductor film occurred at a little bit higher annealing temperature, namely at around 360 degree C, which was confirmed by the photo conductivity measurement.



Figure 4. Photographic image of Sol.P films coated on quartz substrate. The films were pyrolysed at $T_p = 270-420$ °C. Substrate size is 2×2 cm².

(4) Solar cell fabrication [1]

Base on the fundamental studies above, we tried to fabricate a solar cell of which structure is shown in Fig.5. P-type liquid silicon and n-type one were synthesized by UV irradiated ring-opening polymerization with adding decaboran and white phosphorus to CPS as dopants,



Figure 5. Schematic of a solution-processed a-Si:H solar cell structure.

respectively. Table 1 shows the film thickness of each constitutional film with dopant concentration. It was found that film quality was improved by a hydrogen radical treatment by CAT-CVD chamber. Fig.6 shows the properties of the solar cells made from liquid silicon. As the process is not so

Table 1. Thickness and dopant concentrations of the p-, i-, and n-Si layers in cells 1, 2, and 3.

	cell 1	cell 2	cell 3
n-Si: thickness (concentration)	$\frac{30 \text{ nm}}{(2 \times 10^{21} \text{ cm}^{-3})}$	$\begin{array}{c} 30 \text{ nm} \\ (2 \times 10^{21} \text{ cm}^{-3}) \end{array}$	$\begin{array}{c} 30 \text{ nm} \\ (2 \times 10^{21} \text{ cm}^{-3}) \end{array}$
i-Si: thickness	120 nm	120 nm	400 nm
p-Si: thickness (concentration)	$ \begin{array}{r} 30 \text{ nm} \\ (7 \times 10^{21} \text{ cm}^{-3}) \end{array} $	$\frac{30 \text{ nm}}{(1 \times 10^{21} \text{ cm}^{-3})}$	$\begin{array}{c} 30 \text{ nm} \\ (7 \times 10^{20} \text{ cm}^{-3}) \end{array}$

optimized, their properties are not high. With the process



Figure 6. J–V characteristics of the solar cells with the top electrode size of 5_5mm2. The curves denotes by c1, c2, and c3 (c'1, c'2, and c'3) represent the J–V curves for cells 1, 2, and 3 with (without) the hydrogen-radical treatment, respectively. The inset shows the photovoltaic parameters and energy conversion efficiency for cells 1, 2, and 3 with the hydrgen-radical treatment. The curves were measured using the solar simulator under the illumination condition of AM-1.5G (100mW/cm²).

optimization, the higher values would be expected.

Conclusion

A solar cell was successfully fabricated using liquid silicon. Liquid silicon is a solution of polydihydrosilane which is made from cycropentasilane (Si_5H_{10}) by ring-opening polymerization using UV light. Various kinds of the phenomena and properties related to liquid silicon have been scientifically investigated so that the total picture of liquid silicon is now unveiled. That led us to make a solar cell. Although the properties of the developed solar cell are not so high, we think the achievement is a significant step for the future sustainable industry.

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