Model Experiment on the Production of Silicon Droplet

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Cold model experiments were carried out to effectively produce spherical solar cells made of single crystal silicon. Water was used as the working fluid. A single-hole nozzle was chosen to generate water droplets in the dripping mode. The wettability of the nozzle was changed by coating repellent on it. The diameter of a water droplet thus generated depended strongly on the wettability. The flow field in a droplet was visualized with a CCD camera and the velocity vectors were determined with particle image velocimetry. The flow pattern in the droplet was correlated based on the Weber number similitude. A Weber number range suitable for producing single crystal silicon of high quality was found.

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1. Introduction

The use of solar energy is becoming increasingly important. The cost of electrical energy produced by solar cells currently used is much higher than that produced by the conventional systems. Spherical micro solar cells made of single crystal silicon therefore are expected to reduce the cost. The photoelectric transformation efficiency of such spherical solar cells is raised by about four times as large as that of the conventional plate type solar cell, and the initial investment cost is reduced to one third of the conventional one. In addition, the cycle time required for producing the cells is significantly reduced.

A single crystal silicon spherical in shape can be produced with a nozzle in the jetting mode and dripping mode. When molten silicon is dropped through a vertically placed nozzle, molten silicon droplets are successively generated at the exit of the nozzle in the dripping mode and a single crystal silicon is produced due to solidification during its free fall. The single crystal silicon thus produced is polished to become spherical in shape. At present, single crystal silicon sizes of 1 mm in diameter can be produced by this method. In order to enhance the efficiency of the solar cell, much smaller single crystal silicones are expected. Further investigations therefore are required on the generation mechanism of a molten silicon droplet at the nozzle exit.

Many experimental and theoretical model investigations have been carried out for producing liquid droplets, especially focusing on the relationship between the nozzle diameter and the droplet diameter. Previous investigations focused mainly on the droplet generation at a nozzle of good wettability. The materials of the container and nozzle are chosen to be poorly wetted by molten silicon in order to avoid possible chemical reactions with molten silicon. Accordingly, further investigation is required on the effect of the wettability of a nozzle on the droplet generation. The shape and size of a droplet are considered to be functions of (1) the shape and size of a nozzle, (2) the physical properties of molten silicon and gas, (3) the flow rate of molten silicon at the nozzle exit, and (4) the wettability of the nozzle.

Experiment using real molten silicon is rather difficult, and hence, cold model experiments were carried out in this study. The following subjects were mentioned.

(1) The effects of the size of a nozzle and the wettability of the nozzle on the diameter of a liquid droplet.
(2) The effects of the interfacial (or surface) tension and the density difference between a droplet and the fluid enveloping it on the diameter of a droplet.
(3) Calculation of the shape and size of a droplet before detachment from the nozzle with FEM.
(4) Observation of the flow in a droplet with PIV (particle image velocimetry)

2. Experiment

2.1 Relationship between diameter of droplet and nozzle diameter

Figure 1 shows a schematic diagram of the experimental apparatus. Water and silicone oil were used as the working fluids. The kinematic viscosity of the silicone oil, \( \nu_L \), was 1 mm²/s (1 cSt). The physical properties of liquids are listed on Table 1. Droplets of these liquids were successively
generated at the exit of a nozzle placed in the atmosphere. The combinations of the inner and outer diameters of the nozzle were 1.0 mm / C2 6.0 mm, 1.0 mm / C2 8.0 mm, and 2.5 mm × 8.0 mm.

The nozzles were made of glass and wetted both by water and silicone oil. Each nozzle was coated with repellent to change its wettability. The wettability was evaluated in terms of the contact angle. Figure 2 shows a liquid droplet placed on a solid plate, where \( \theta_c \) is the contact angle. The solid is wetted by the liquid for \( 0 \leq \theta_c < 90^\circ \), while it is poorly wetted by the liquid for \( 90^\circ \leq \theta_c \leq 180^\circ \). Gas attaches preferably to a solid body of poor wettability. The contact angles of the nozzle thus changed are listed in Table 2.

Experiments were carried out at a constant temperature of 25°C (298 K). The contact angle for a water droplet placed on the original glass surface was 74°, and 145° on the fluoro-resin-coated surface. Meanwhile, for a silicone oil droplet, \( \theta_c \) was 20° on the original glass surface and 21° on the fluoro-resin-coated surface.

### 2.2 Flow pattern in liquid droplet

Figure 3 shows a schematic diagram of the experimental apparatus for flow pattern measurements in a water droplet. It was generated at the exit of a nozzle placed in a silicone oil bath or an n-pentane bath. The kinematic viscosities of silicone oils were 1,10,100,1000 mm²/s (cSt) and that of n-pentane was 0.36 mm²/s, as can be seen in Table 1. Nozzles made of glass were used. One nozzle had an inner diameter \( d_{ni} \) of 1.0 mm and an outer diameter \( d_{no} \) of 8.0 mm, the other had \( d_{ni} \) of 2.5 mm and \( d_{no} \) of 8.0 mm. Tracer particles of a mean diameter of 11 μm (Vinylidene acrylonitride chloride: \( \rho = 1.04 \text{ g/cm}^3 \)) was mixed in water to visualize the flow in a water droplet. The measurement method is described as follows:

1. The exit of the nozzle was immersed in the bath. The flow rate of water was adjusted with a cock and the water was supplied into the nozzle. The liquid temperatures were kept at 25°C.
2. A vertical laser sheet was generated to pass the centerline of the nozzle, so that the inner part of a water droplet growing at the nozzle exit was visualized. Images of tracers in the droplet were recorded with a CCD camera and stored on a personal computer.
3. The velocity vectors in the droplet were determined with particle image velocimetry (PIV). The recorded images were processed by using the cross-correlation method.
4. The shape and size of the water droplet were simultaneously observed with a high-speed video camera at 500 frames/s.
3. Numerical Calculation of the Shape and Size of a Growing Water Droplet

The shape and size of a water droplet growing at the nozzle exit under a quasi-static condition was calculated by use of the finite element method (FEM). The energy of the droplet can be expressed by

$$F = \frac{\pi}{2}(\rho_L - \rho_g)g \int_0^{\pi/2} R^2 \cos \theta \sin \theta d\theta$$

(Potential energy)

$$+ 2\pi \gamma_{Lg} \int_0^{\pi/2} R \sqrt{R^2 + R_o^2} \sin \theta d\theta$$

(Liquid-gas surface energy)

$$+ \pi \gamma_{Lg} \cos \theta \frac{D^2 - d_{m}^2}{4}$$

(Solid-gas surface energy)

$$+ \lambda \left( V_d - \frac{2}{3} \pi \int_0^{\pi/2} R^3 \sin \theta d\theta \right)$$

(1)

where $\rho_L$ is the density of liquid, $\rho_g$ is the density of gas, $g$ is the acceleration due to gravity, $\gamma_{Lg}$ is the surface tension, $D$ is the bottom diameter of the droplet, $\lambda$ is the Lagrangian multiplier, and $V_d$ is the volume of the droplet given a priori. Other symbols are shown in Fig. 4. In calculating the shape and size of a water droplet growing in a liquid bath, the density of that liquid was substituted into $\rho_g$ in eq. (1).

By minimizing the fourth term on the right-hand side of eq. (1), the shape and size of a droplet can be determined for a given $V_d$ value.

4. Experimental Results and Discussion

4.1 Effect of the wettability of nozzle edge on the formation of water droplet

The shape of a water droplet growing at the nozzle exit placed in the atmosphere was significantly affected by the wettability of the nozzle edge, as shown in Fig. 5. When the edge is wetted by water, the bottom of a water droplet extends to the position of the outer diameter of the nozzle. On the other hand, the bottom of a water droplet generated at a nozzle of poor wettability is constricted by an inner diameter of the nozzle. The diameter of a droplet growing at a wetted nozzle was independent of the inner diameter of the nozzle, while that of a droplet growing at a poorly wetted nozzle was independent of the outer diameter of the nozzle.

4.2 Comparison of the diameter of falling droplet between experiment and empirical calculation

For every nozzle the diameter of a falling droplet, $d_p$, remained constant until the flow rate, $Q_L$, reached a certain critical value. The detail of the critical value will be

![Figure 4: Pendent droplet.](image)

![Figure 5: Droplets at nozzle exits of good and poor wettability.](image)
explained in the next section. Ten droplets were collected for measuring a mean mass of a droplet. The droplet was assumed to be spherical in shape and its diameter, $d_p$, was determined. Satellite droplets were not counted for measuring the mean mass because the volume of a satellite droplet is less than 3% of the volume of a droplet.\textsuperscript{25}) Figure 6 shows that the measured value of the diameter is smaller for the poorly wetted nozzle than for the wetted nozzle. This is because the bottom of a droplet growing at the nozzle exit of good wettability spreads towards the outer diameter of the nozzle. Accordingly, it is more effective for producing smaller droplets to use a nozzle of poor wettability. Figure 7 shows that a silicone oil droplet is much smaller than a water droplet. The shape of a droplet is not affected by flow rate, $Q_L$, under the critical flow rate.

The measured values shown in Fig. 6 are non-dimensionalized by the nozzle diameter, $d_n$, and re-plotted against the following Bond number, $Bo$, in Fig. 8. The measured values obtained for a flow rate greater than the critical flow rate are omitted.

$$\text{Bo} = \frac{\Delta \rho g d_n^2}{\gamma L}$$

where $\Delta \rho$ is the density difference between liquid and gas. In this arrangement, the inner diameter, $d_{ni}$, is substituted for $d_n$ when the nozzle is poorly wetted by liquid, while the outer diameter, $d_{no}$, is substituted for $d_n$ when the nozzle is wetted by the liquid. It is evident that the measured values are satisfactorily correlated by this arrangement method, regardless of the wettability of the nozzle. The following empirical equation, proposed by Ohtake et al.,\textsuperscript{3)} can predict all the values measured under the critical flow rate.

$$\frac{d_p}{d_n} = 1.62\frac{\gamma_{li}/(\Delta \rho g d_n^2)^{1.35}}{}$$

The nozzle end: Glass
\begin{align*}
\text{Glass} & : 2.5 \text{mm} \\
\text{Silicone oil – Air} & : 8.0 \text{mm} \\
Q_L & : 0.01 \text{ml/s}
\end{align*}

The nozzle end: Glass
\begin{align*}
\text{Glass} & : 2.5 \text{mm} \\
\text{Water – Air} & : 8.0 \text{mm} \\
Q_L & : 0.02 \text{ml/s}
\end{align*}

Fig. 6 Relationship between droplet diameter and nozzle diameter.

Fig. 7 Droplets of silicone oil and water.
4.3 Length of droplet just before detachment from nozzle

The length of a droplet, $H$, just before detachment from a nozzle was divided by the nozzle diameter, $d_n$, and plotted against the Bond number, $Bo$, in Fig. 9. The measured values of $H/d_n$ were approximated by the numerical value based on FEM which was indicated by the solid line. Concerning $d_n$, the same treatment as explained on Fig. 8 must be done. Figure 10 shows the dimensionless length of a droplet, $H/d_{ni}$, and a modified Weber number, $We'$, for $Bo = 0.82$.

$$We' = \frac{\rho_L Q_L v_n}{7 g d_{ni}^2} \times \frac{\Delta \rho}{\rho_L}$$  \hspace{1cm} (4)

where $Q_L$ is the water flow rate, $v_n$ is the velocity of water at the nozzle exit, and $\Delta \rho (= \rho_L - \rho_g)$ is the density difference.

The measured values of $H/d_n$ agreed well with the numerical value when $We'$ is small but becomes greater than the numerical value as $We'$ exceeds approximately 0.042. Namely, a droplet becomes longer in the vertical direction with an increase in the inertial force of water issuing into the droplet.

The above-mentioned results mean that the numerical simulation based on FEM is valid when the water flow rate is low ($We' < 0.042$).

4.4 Formation of satellite droplet

Figures 11 and 12 show falling water droplets for wetted and poorly wetted nozzles, respectively. The images are not clear because they were taken by a high speed video camera. In Fig. 12, a small droplet can be seen behind a large droplet. The small droplet was generated due to breakup of a liquid filament and called a satellite droplet. Such a satellite droplet was not generated when the Bond number, $Bo$, was less than 0.130. Ishido et al.\textsuperscript{21} reported that a satellite droplet is not observed for $Bo < 0.064$. However, they did not carry out an experiment for $Bo > 0.064$.

4.5 Effect of the physical properties of liquid in a bath on the formation of droplet

4.5.1 Effect of kinematic viscosity of liquid

As mentioned in the preceding section, the shape of a water droplet just before detachment from the nozzle exit departs from the numerical one with an increase in the liquid flow rate, $Q_L$. The critical value of the modified Weber number, $We'$, was 0.042 in a water-air system. The effect of the kinematic viscosity of silicone oil contained in the bath (see Fig. 3) on the critical liquid flow rate or critical modified Weber number was investigated. The measurements were carried out for silicone oils of three kinematic viscosities. Figure 13 reveals that the effect of the kinematic viscosity is negligibly small under the present experimental conditions and the critical modified Weber number is 0.042.
Fig. 11 Falling droplet accompanied by satellite droplet.

Nozzle end: Glass
- $d_{nl}: 1.0\text{mm}$
- $d_{no}: 8.0\text{mm}$
Silicone oil – Air
- $Q_L: 0.01\text{ml/s}$

Fig. 12 Falling droplet without satellite droplet.

Nozzle end: Fluororesin
- $d_{nl}: 1.0\text{mm}$
- $d_{no}: 8.0\text{mm}$
Water – Air
- $Q_L: 0.005\text{ml/s}$
4.5.2 Effect of density of liquid in the bath on the formation of droplet

In order to investigate the effect of the density of liquid in the bath on the formation of a water droplet, n-pentane was chosen as a liquid in the bath. Figure 14 shows the height of a water droplet in the n-pentane bath. The effect of the inertial force of water issuing out of the nozzle appears when the modified Weber number $W_{e'}$ exceeds 0.042. For $W_{e'} < 0.042$, a water droplet grows at the nozzle exit in a quasi-static manner.

4.6 Flow pattern in water droplet

Figures 15(a) and (b) show velocity vectors and the flow pattern in a water droplet growing in a silicone oil bath, respectively. The flow patterns in the droplet shift from Type A to Type D with an increase in the water flow. In Type A,
the water flow in the water droplet was very slow and most water entering into the droplet dispersed in the radial direction before reaching the top of the droplet. In Type B, the velocity of water around the vertical axis of the droplet was high and a recirculation region was formed in the whole droplet. In Type C, the scale of the recirculation region became small and it was localized near the top of the droplet. Finally, in Type D, the flow in the droplet became unstable and some vortices were generated in the droplet. Type D was observed for \( \text{We}^* > 0.042 \), as can be seen in Fig. 16.

Concerning the droplet formation in an n-pentane bath, Type B and Type C were not observed, as can be seen in Fig. 17. This is explained by the fact that a water droplet generated in the n-pentane bath becomes slender \((W/d_{ni} = 1.9)\) than the value \((W/d_{ni} = 4.4)\) in the silicone oil bath. The recirculation region is therefore not formed in the droplet.

Figures 16 and 17 mean that the flow pattern in a droplet for \( \text{We}^* < 0.042 \) is governed by the Bond number, \( \text{Bo} \), in addition to the modified Weber number, \( \text{We}^* \). This is explained in Fig. 18.29) Types A, B, and C were observed for \( \text{Bo} < 0.25 \) and \( \text{We}^* < 0.042 \). Only type A was observed for \( 0.25 \lesssim \text{Bo} \lesssim 24 \) and \( \text{We}^* < 0.042 \). Droplets were not generated for \( \text{Bo} \gtrsim 24 \) and \( \text{We}^* \lesssim 0.06 \).

5. Conclusions

Main findings obtained in this study can be summarized as follows:

(1) A water droplet grows in a quasi-static manner at the nozzle exit until the modified Weber number, \( \text{We}^* \), exceeds 0.042. The shape and size of a water droplet just before detachment form the nozzle are satisfactorily predicted by numerical simulation based on FEM. A water droplet becomes slender with an increase in \( \text{We}^* \) for \( \text{We}^* > 0.042 \).

(2) The diameter, \( d_p \), of a water droplet falling in the atmosphere can be predicted by the following empirical equation:

\[
d_p/d_n = 1.62\left[\frac{\gamma_{ls}}{(\Delta \rho g d_n^2)}\right]^{0.35}
\]

The inner diameter of the nozzle, \( d_{ni} \), should be substituted for \( d_n \) when the nozzle is poorly wetted by water, whereas the outer diameter, \( d_{no} \), should be substituted for \( d_n \) when the nozzle is wetted by water.

(3) Satellite droplets are not generated when the Bond number, \( \text{Bo} \), is smaller than 0.130.

(4) The flow pattern in a water droplet can be classified into four types, A, B, C, and D. The type changes from A to D with an increase in the modified Weber number, \( \text{We}^* \). Type D appears for \( \text{We}^* > 0.042 \). The flow patterns in Type A, B, and C are axis-symmetrical with respect to the vertical axis of the water droplet. The flow in the droplet in Type D was unstable, and accordingly, water droplets classified into this type is not suitable for producing single crystal silicon.
Nomenclature

\( Bo \): Bond number
\( d_n \): nozzle diameter
\( d_{ni} \): inner nozzle diameter
\( d_{no} \): outer nozzle diameter
\( g \): acceleration due to gravity
\( Q_w \): water flow rate
\( V_d \): volume of droplet
\( v_n \): velocity of water at the nozzle exit
\( We_0 \): modified Weber number
\( \Delta \rho \): density difference
\( \gamma_{LI} \): interfacial tension
\( \nu_L \): kinematic viscosity of liquid
\( \theta_c \): contact angle
\( \rho_g \): density of gas
\( \rho_L \): density of liquid

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