



P15

Ge 融体の表面張力に及ぼす表面酸素分圧の影響

Effect of Surface Oxygen Partial Pressure on Surface Tension of Liquid Germanium

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1. Introduction

In order to develop and optimize the fabrication process of Si-Ge semiconductor, accurate values of the surface tension and its temperature coefficient are required. Surface tension is one of the most important parameters to decide a meniscus angle and wetting behavior. Temperature coefficient of surface tension is crucial to explain a heat and mass transportation phenomena through the thermal Marangoni effect that appears at liquid surface. Therefore, the measurement of surface tension of liquid Si-Ge alloys was carried out at the international space station (ISS) as a part of the international collaboration called "SEMITHERM" (investigation of Semiconductor Thermophysical Properties at the ISS). However, the influence of oxygen partial pressure on surface tension was considered in the measurement though oxygen is well known as strong surfactant for liquid metals.

Ratto, Ricci, and Arato (RRA) proposed a theoretically derived model that oxygen partial pressure in vicinity of liquid surface ($P_{O_2}^{sur}$) becomes extremely lower than that of bulk gas for liquid sample forming volatile oxides ¹⁾. Our group was experimentally confirmed the validity of the RAA model for liquid silicon ²⁾.

In the present study, the validity of the RRA model was experimentally examined for liquid germanium through the in-situ observation of oxidation/reduction behavior of the liquid surface using the electromagnetic levitation (EML) technique. Surface tension of liquid germanium was measured under contamination free condition form contain by using the EML together with the RRA model. The purpose of this study was to clarify the influence of $P_{O_2}^{sur}$ on the surface tension of liquid germanium as a basic data to discuss and evaluate the results of the ISS experiment.

2. Experimental method

A cubic of non-doped germanium was chemically cleaned by using a 1:3 mixture of HF and HNO₃, and then placed on a quartz holder position in the EML coil. The sample was preheated using a semiconductor laser beam to give it sufficient conductivity under a high purity mixture of argon and helium gas flowing at 2L/min. After the sample was electromagnetically levitated and melted, its temperature was controlled by varying the output power of the laser and the partial pressures of argon and helium gases. A monochromatic pyrometer was used to monitor the sample. Furthermore, oxygen partial pressure of the inlet gas ($P_{O_2}^{in}$) of the Ar-He was adjusted by mixing oxygen gas and monitored with a zirconia oxygen sensor operated at 1008 K to control $P_{O_2}^{sur}$ according to the RRA model. The $P_{O_2}^{sur}$ calculated by the RRA model was controlled to be either slightly above or below the equilibrium oxygen partial pressure for forming GeO₂(s), $P_{O_2}^{GeO_2}$. The oxidation and reduction of the droplet was observed for several minutes using a high-speed video (HSV) camera and pyrometer to investigate if the $P_{O_2}^{sur}$ was actually higher or lower than the $P_{O_2}^{GeO_2}$ to experimentally evaluate the

validity of the RRA model. If $\text{GeO}_2(\text{s})$ is formed, the droplet image brightens due to its higher emissivity, which can be detected by the pyrometer.

For the reduced droplet, the frequencies of the surface oscillations of the $m = 0, \pm 1$, and ± 2 for the $l = 2$ mode, and those of the center of gravity were analyzed from time-sequential data of the HSV images. The influence of the apparent rotations was considered in the analysis as well as that of the real rotation. The surface tension of liquid germanium was calculated from these frequencies using Rayleigh equation ³⁾ calibrated by Cummings and Blackburn ⁴⁾. The density of the liquid germanium, ρ_{Ge} , used in the calculation was determined from the following equation, reported by Mizuno *et al.* ⁵⁾.

$$\rho(T) = 5616 - 0.508(T - 1211) \text{ [kg} \cdot \text{m}^{-3}] \quad (1)$$

3. Results and Discussion

Figure 1 shows the experimental result of in-situ observation for the oxidation and reduction behavior of the levitated germanium under a flowing mixture of Ar-He- O_2 gas, at which the calculated value of $P_{\text{O}_2}^{\text{sur}}$ was controlled to be slightly higher or lower than the thermodynamically calculated reference value of $P_{\text{O}_2}^{\text{GeO}_2}$ shown by a solid line. The closed circle (●) and open circle (○) plots correspond to the experimental results that oxidation and reduction of the levitated germanium droplet was observed, respectively. Typical HSV images of the (a) oxidized and (b) reduced droplets are also shown. When the calculated $P_{\text{O}_2}^{\text{sur}}$ is less than the reference $P_{\text{O}_2}^{\text{GeO}_2}$ value, no oxidation was detected in the temperature profile and HSV images of the droplet. Whereas oxidation of liquid surface was clearly detected through an increase in the emissivity of the sample, when the calculated value of $P_{\text{O}_2}^{\text{sur}}$ becomes slightly more than the reference $P_{\text{O}_2}^{\text{GeO}_2}$ value. This confirms that the RRA model can evaluate $P_{\text{O}_2}^{\text{sur}}$ comparatively well for liquid germanium.

Since the RRA model was experimentally validated to evaluate the $P_{\text{O}_2}^{\text{sur}}$ of germanium, surface tension of liquid germanium was measured as functions of temperature and $P_{\text{O}_2}^{\text{sur}}$, at which the $P_{\text{O}_2}^{\text{sur}}$ was fixed at almost a constant value of $P_{\text{O}_2}^{\text{sur}} \approx 10^{-6} \text{ Pa} - 10^{-11} \text{ Pa}$. The surface tension of liquid germanium is successfully measured over a very wide temperature range from about 1380 K to 2310 K. The temperature dependence of surface tension of liquid germanium shows almost the same value regardless of the $P_{\text{O}_2}^{\text{sur}}$. The surface tension linearly decreases with increasing temperature above 1600K, which is expressed using a least-square approach for the plots as follows,

$$\sigma(T) = 635 - 0.118(T - 1211) \text{ [} 10^{-3} \text{N} \cdot \text{m}^{-1} \text{]} (1600 \text{ K} < T < 2400 \text{ K}) \quad (2)$$

However, the surface tension becomes lower than the extrapolated value of this line when the sample temperature is below 1600 K. Since equilibrium constant of oxygen adsorption reaction should be increase at low temperature, oxygen adsorption may induce a decrease in the surface tension of liquid germanium below 1600 K.

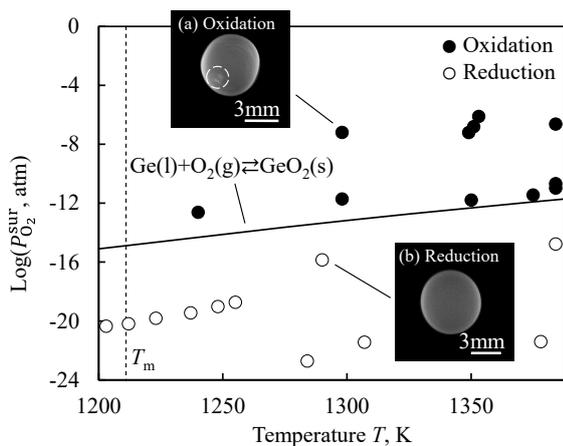


Fig. 1 Behaviors of oxidation and reduction of germanium droplet levitated by EML under various values of calculated $P_{\text{O}_2}^{\text{sur}}$ by the model of Ratto, Ricci and Arato ¹⁾.

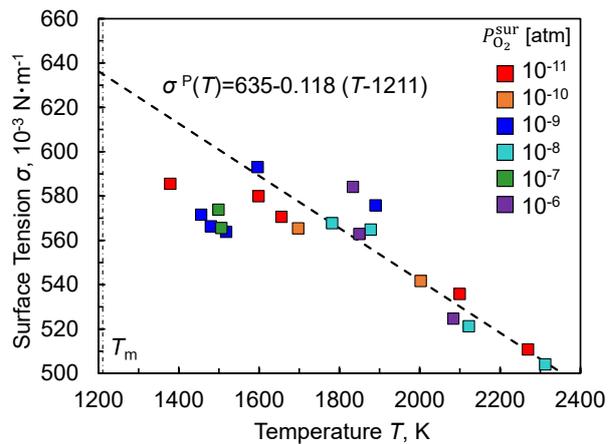


Fig. 2 The surface tension of liquid germanium as functions of temperature and $P_{\text{O}_2}^{\text{sur}}$

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