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電磁浮遊法による表面酸素分圧を考慮したゲルマニウム融体の表面張力測定

Surface Tension Measurement of Germanium Melt Considering Surface Oxygen Partial Pressure by Electromagnetic Levitation Method

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1. Introduction

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 named "SEMITHERM" (investigation of Semiconductor Thermophysical Properties at the ISS). However, the effect of oxygen adsorption on the surface tension from the atmospheric gas was not considered in the measurement though oxygen is strong surfactant for liquid metallic melt. The effect of oxygen Arato *et al.* proposed a theoretically derived model in which oxygen partial pressure in vicinity of liquid surface ($P_{O_2}^{sur}$) would be lower than that of bulk gas when the liquid sample can form volatile oxides [1]. The validity of their model was experimentally confirmed for liquid silicon by our group using the oscillating droplet method using the electromagnetic levitation (EML) technique [2].

In the present study, we measured surface tension of liquid germanium by the EML, based on the measurement results on the surface tension of liquid silicon. The $P_{O_2}^{sur}$ at the measurement was calculated by the model by Arato *et al*. The purpose of this study was to measure accurate the surface tension of liquid germanium in consideration of oxygen adsorption from the measurement atmosphere.

2. Experimental method

A cube of high purity germanium, chemically cleaned by using a 1:3 mixture of HF and HNO_3, was preheated in the EML chamber using a semiconductor laser beam to give it sufficient conductivity under a high purity mixture of argon and helium gas flowing at 2 L/min. After the sample was electromagnetically levitated and then completely 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 measure the sample temperature. 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 type oxygen sensor operated at 1008 K to control $P_{O_2}^{sur}$ below the equilibrium oxygen partial pressure for formation of GeO_2 according to the model of Arato *et al*. The oscillation behavior of the droplet was monitored by a high-speed video (HSV) camera. The frequencies of the surface oscillations of the m = 0, ±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 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].

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

3. Results and Discussion

Surface tension of liquid germanium was measured over a wide temperature range from 1379 to 2270 K at $P_{O_2}^{sur}$ of the orders of 10^{-6} (■), 10^{-4} (■), and 10^{-2} (■) Pa. The results are shown in Figure 1, along with some literature data. Figure 2 shows the relationship between the $P_{O_2}^{sur}$ and temperature corresponding to the measurement plots of surface tension of Figure 1, compared with the equilibrium oxygen partial pressure for oxidation reaction of liquid germanium into germanium (IV) oxide (GeO_2). When $P_{O_2}^{sur}$ was controlled to be lower than the equilibrium oxygen partial pressure for oxidation reaction of liquid germanium into GeO_2, the temperature dependence of the surface tension was almost the same regardless of $P_{O_2}^{sur}$; the surface tension decreases linearly with elevating temperature above 1700 K. This indicates that the surface tension of liquid germanium measured at above 1700 K is in pure state value, $\sigma_{Ge}^{P}(T)$, which is free from any contaminations such as oxygen adsorption and chemical reaction with the supporting material. The $\sigma_{Ge}^{P}(T)$ can be extrapolated to lower temperature by using a least-squares method from the measurement plots at high temperature as shown by a dashed line.

When the measurement was carried out below 1700 K, the surface tension becomes lower than the $\sigma_{Ge}^{P}(T)$ regardless of $P_{O_2}^{sur}$. Furthermore, the surface tension measured at the orders of 10^{-6} (■) Pa and 10^{-4} (■) Pa are almost the same. These results would be attributed to the formation of liquid GeO_2 on liquid surface because the $P_{O_2}^{sur}$ is higher than the equilibrium oxygen partial pressure for oxidation reaction of liquid germanium into GeO_2. Since liquid GeO_2 can finely disperse on liquid surface, being different from solid state, it would not be detected in HSV images.

Several literature data being lower than the $\sigma_{Ge}^{P}(T)$ obtained in this study may be due to the formation of liquid GeO_2 on liquid surface, because they were measured under $P_{O_2}^{sur}$ that liquid GeO_2 should be formed in the equilibrium state.

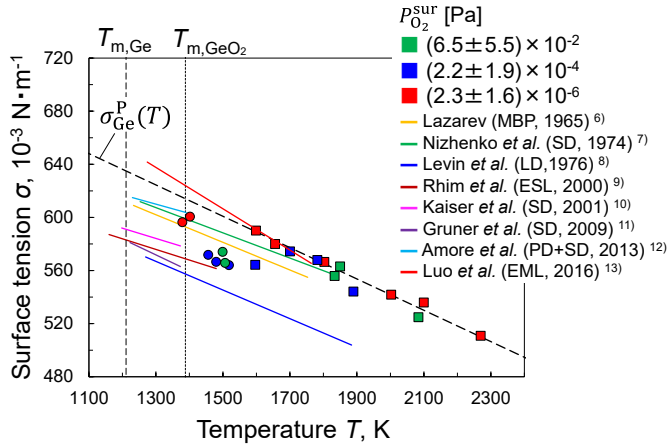

Figure 1. Relationship between surface tension and temperature of liquid germanium and liquid germanium oxide

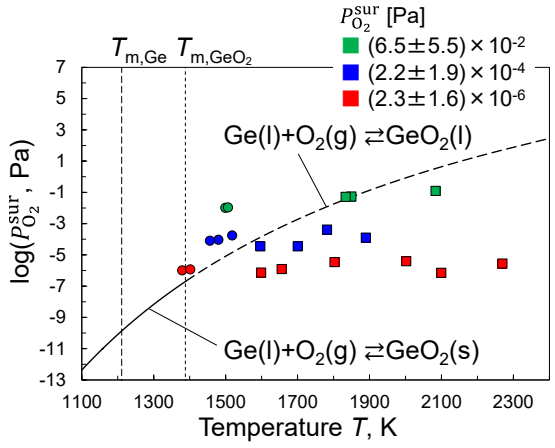

Figure 2. The relationship between $P_{O_2}^{sur}$ and temperature corresponding to each measurement plot

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References

1) M. Ratto, E. Ricci and E. Arato: Mechanism of oxidation/deoxidation of liquid silicon: theoretical analysis and interpretation of experimental surface tension data. J. Cryst. Growth, **217** (2000) 233, DOI: 10.1016/S0022-0248(00)00496-6.
2) S. Ozawa, Y. Nagasaka, M. Itakura, K. Sugisawa and Y. Seimiya: Influence of oxygen adsorption from atmosphere on surface tension of liquid silicon. J. Appl. Phys., **130** (2021) 135101, DOI: 10.1063/5.0062062.
3) Lord Rayleigh: On the Capillary Phenomena of Jets. Proc. R. Soc. Lond., **29** (1879) 71, DOI: 10.1098/rspl.1879.0015.
4) D.L. Cummings, D.A. Blackburn: Oscillations of magnetically levitated aspherical droplets. J. Fluid Mech, **224** (1991) 395, DOI: 10.1017/s0022112091001817.
5) A. Mizuno, H. Kawauchi, M. Tanno, K. Murai, H. Kobatake, H. Fukuyama, T. Tsukada and M. Watanabe: Concentration Dependence of Molar Volume of Binary Si Alloys in Liquid State. ISIJ International, **54** (2014) 2120, DOI: 10.2355/isijinternational.54.2120.
6) V.B. Lazarev: Surface phenomena in alloyed germanium metals. Russ. J. Phys. Chem., **39** (1965) 36, DOI: 10.1007/BF00854880.
7) V.I. Nizhenko, L.I. Floka: Surface properties of Fe-Ge metals. Russ. Metal, **6** (1975) 68.
8) E.S. Levin, V.N. Zamaraev, M.S. Petrushevskii, P.V. Gel'd and A.P. Timofeev: Density and Surface Energy of Liquid Germanium-Manganese Alloys. Russ. J. Phys. Chem., **50** (1976) 1648.
9) W.K. Rhim and T. Ishikawa: Thermophysical Properties of Molten Germanium Measured by a High-Temperature Electrostatic Levitator, Int. J. Thermophys, **21** (2000) 429, DOI: 10.1023/A:1006639714415.
10) N. Kaiser, A. Croll, F.R. Szofran, S.D. Cobb and K.W. Benz: Wetting angle and surface tension of germanium melts on different substrate materials. J. Cryst. Growth, **231** (2001) 448, DOI: 10.1016/S0022-0248(01)01480-4.
11) S. Gruner, M. Köhler1 and W. Hoyer: Surface tension and mass density of liquid Cu–Ge alloys. J. Alloys Compd., **482** (2009) 335, DOI: 10.1016/j.jallcom.2009.04.005.
12) S. Amore, D. Giuranno, R. Novakovic, E. Ricci, R. Nowak and N.S. obczak: Thermodynamic and surface properties of liquid Ge–Si alloys. CALPHAD, **44** (2014) 95, DOI: 10.1016/j.calphad.2013.07.014.
13) Y. Luo, B. Damaschke, S. Schneider, G. Lohöfer, N. Abrosimov, M. Czupalla and K. Samwer: Contactless processing of SiGe-melts in EML under reduced gravity. npj Microgravity, **2** (2016) 1, DOI: 10.1038/s41526-016-0007-3.