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# Ellipsometric study of the prewetting transition at the mercury–sapphire interface

Yoshinori Ohmasa, Yukio Kajihara and Makoto Yao
Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

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**Abstract.** Optical reflectivity measurements were carried out on fluid mercury against an optically transparent sapphire window at high temperatures and pressures up to 1550 °C and 180 MPa. In order to make quantitative analyses, we performed not only normal-reflection measurements but also ellipsometric measurements with 45°-reflection geometry, and the occurrence of the prewetting transition was confirmed clearly.

## 1. Introduction

Under ambient conditions, liquid mercury is a non-wetting substance on solid non-metallic substances, and forms drops on glass, quartz and sapphire. For such a situation, it is expected from Cahn's critical-point wetting theory [1] that a wetting transition will take place at high temperatures and high pressures close to the liquid–vapour critical point of mercury ($T_c = 1478$ °C, $p_c = 167$ MPa, $d_c = 5.8$ g cm$^{-3}$). In 1996, Yao and Hensel found that reflectivity experiments on fluid mercury against a sapphire surface reveal the existence of a prewetting transition of mercury on a sapphire substrate [2]. They observed that the prewetting line intersects the coexistence curve at the wetting temperature $T_w = 1310$ °C, and terminates at the prewetting critical temperature $T_{pw}^c = 1468$ °C and prewetting critical pressure $p_{pw}^c = 158.6$ MPa, lying close to the bulk critical point.

In the present work, optical reflectivity measurements were carried out on fluid mercury against an optically transparent sapphire window at high temperatures and pressures up to 1550 °C and 180 MPa, and confirmed the occurrence of the prewetting transition. In order to make more quantitative analyses, we performed not only normal-reflection measurements but also ellipsometric measurements with 45°-reflection geometry. These data are useful for determining the layer thickness $l$ accurately, as well as the bulk complex refractivity, $n + \mathrm{i}k$.

## 2. Experimental procedure

We have performed optical reflectivity measurements on a sapphire–mercury interface with normal-reflection and 45°-reflection geometry. A He–Ne laser (wavelength $\lambda = 632.8$ nm) was used as a light source. Single-crystalline sapphire rods with diameters of 6 mm were used as optical windows. In order to measure the reflectivity for the normal-reflection geometry, $R_n$, a sapphire rod which has a flat surface perpendicular to the axis of the rod was used. In the 45°-reflection measurements, we used a wedge-shaped sapphire rod as

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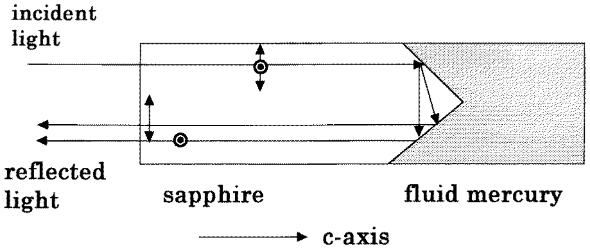

**Figure 1.** A sketch of the set-up for the 45°-reflection measurement. A wedge-shaped sapphire rod was used.

shown schematically in figure 1. The axis of the rod was parallel to the optical axis (the *c*-axis) of the sapphire crystal. The angle between the two surfaces of the wedge was 90°. When the light is incident along the axis of the rod, it is reflected successively by the two surfaces, and the reflected light goes back through the sapphire rod.

The main problem in the application of ellipsometry to high-temperature and high-pressure experiments is the determination of the phase shift. Since it is strongly affected by the birefringence of the sapphire window, and the birefringence is highly temperature dependent, it is difficult to derive the contribution from the sapphire–mercury interface. In order to avoid this difficulty, we measured the amplitude of the reflectivity for p- and s-polarized light, $R_p$ and $R_s$, respectively, instead of the reflectivity ratio $\rho = r_p/r_s = \tan\psi\exp(\mathrm{i}\delta)$.

Because of the birefringence of the sapphire crystal, the wedge-shaped sapphire rod works as a polarizing prism. The reflected light split into two beams, which are orthogonally linearly polarized, namely, p- and s-polarized. This enables us to measure $R_p$ and $R_s$ separately. The sapphire rod was inserted into a molybdenum cell, which was filled with fluid mercury. The cell assembly, together with two heaters, was set in a steel high-pressure vessel which was pressurized with argon gas.

## 3. Results and discussion

First, we measured the reflectivity of fluid mercury far from the liquid–gas coexistence curve, and estimated the bulk complex refractive index $\tilde{n} = n + \mathrm{i}k$ as a function of the density $d$ of the fluid mercury. When there is no wetting layer, the reflectivity from the sapphire–mercury interface for the normal incidence ($R_n$), for the s-polarized light ($R_s$) and for the p-polarized light ($R_p$) in the 45°-reflection geometry can be written as [3]

$$R_n = |r_n|^2 = \left|\frac{n_0 - \tilde{n}}{n_0 + \tilde{n}}\right|^2 \tag{1$a$}$$

$$R_s = |r_s|^2 = \left|\frac{n_0 - \sqrt{2\tilde{n}^2 - n_0^2}}{n_0 + \sqrt{2\tilde{n}^2 - n_0^2}}\right|^2 \tag{1$b$}$$

$$R_p = |r_s|^2 = \left|\frac{\tilde{n}^2 - n_0\sqrt{2\tilde{n}^2 - n_0^2}}{\tilde{n}^2 + n_0\sqrt{2\tilde{n}^2 - n_0^2}}\right|^2 \tag{1$c$}$$

respectively. Here $n_0 = 1.77$ is the refractive index of sapphire. From equations (1*b*) and (1*c*), one can see that the relation $R_p = R_s^2$ always holds for 45° reflection. Therefore we need both $R_n$ and $R_p$ $(=R_s^2)$ to derive the two unknown parameters $n$ and $k$.

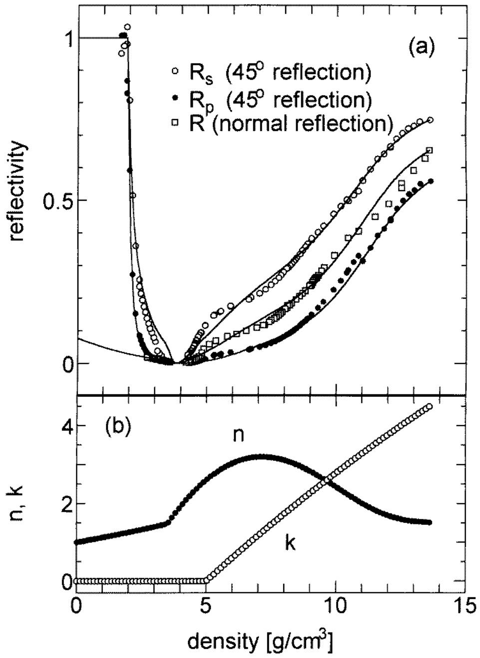

**Figure 2.** (a) The symbols show the observed reflectivity of the bulk mercury against the sapphire window. The solid diamonds show the reflectivity for the normal incidence ($R_n$), while the open circles and closed circles show the reflectivity for the s-polarized light ($R_s$) and for the p-polarized light ($R_p$) in the 45°-reflection geometry, respectively. The solid lines show the reflectivity calculated from $n$ and $k$ shown in (b). (b) The estimated $n$ and $k$ as functions of the density.

Figure 2(a) shows the observed reflectivities $R_n$, $R_s$ and $R_p$. Below $d = 2.0$ g cm$^{-3}$, $R_s$ and $R_p$ are nearly equal to unity, which implies that $n$ is less than $n_0/\sqrt{2}$ in this region, and total reflection occurs for 45°-reflection geometry. Around $d = 3.8$ g cm$^{-3}$, the reflectivity is very small, indicating that $n$ is close to $n_0$.

In the present work, we assumed that $n$ and $k$ depend only on the density. In the low-density region ($d \leqslant 3.5$ g cm$^{-3}$), the reflectivity is well explained by assuming that $k$ is zero and $n$ can be calculated from the Clausius–Mossotti (C–M) relation

$$n = \sqrt{\frac{1 + 2\alpha d}{1 - \alpha d}} \tag{2}$$

where $\alpha$ is a number proportional to the polarizability of an isolated atom. In the present work, $\alpha$ is estimated to be 0.081. In the higher-density region, $n$ and $k$ were expanded in powers of the density, and the expansion coefficients were adjusted to fit the calculated reflectivity to the observed one. At the density of 13.6 g cm$^{-3}$, $n$ and $k$ are fixed to the values of reference [4]. Figure 2(b) shows the estimated $n$ and $k$ as functions of the density. These $n$ and $k$ approximately reproduce the density dependencies of $R_n$, $R_s$ and $R_p$ as shown by the solid lines in figure 2(a).

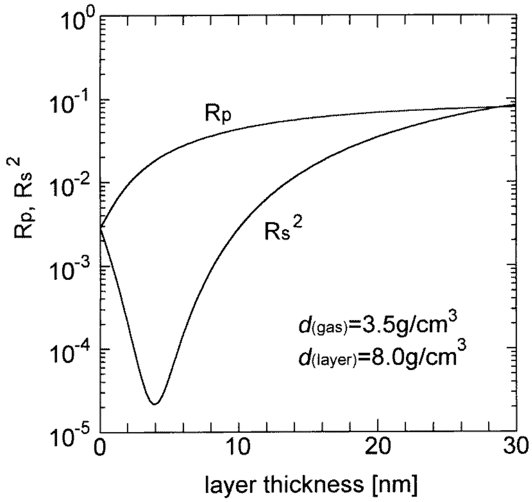

**Figure 3.** The calculated reflectivity for the s-polarized light ($R_s$) and that for the p-polarized light ($R_p$) in 45°-reflection geometry in the case where a wetting layer is present on the sapphire–mercury interface. They were calculated as functions of the layer thickness for a typical case in which the density of the wetting layer is 8 g cm$^{-3}$ and the density of the coexisting gas is 3.5 g cm$^{-3}$.

When the wetting layer is present, $R_n$, $R_s$ and $R_p$ are expressed in terms of the complex refractive index of the wetting layer, $\tilde{n}_l = n_l + \mathrm{i}k_l$, and the layer thickness. The most important thing is that, when the wetting layer is present, the relation $R_p = R_s^2$ does not hold any more. As an example, figure 3 shows how the $R_p$ and $R_s^2$ depend on the layer thickness. Here we have assumed a typical case in which the density of the wetting layer is 8 g cm$^{-3}$

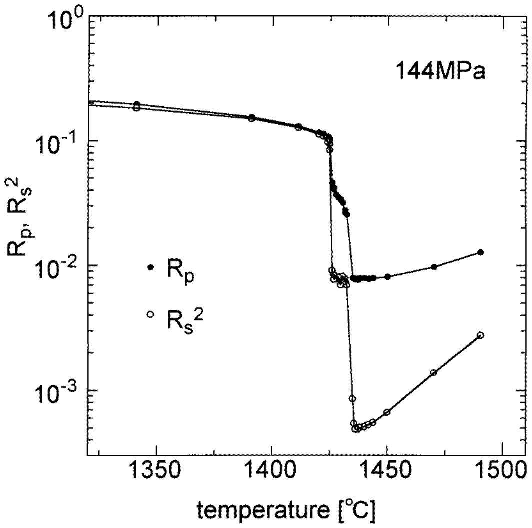

**Figure 4.** Representative results for $R_p$ and $R_s^2$ observed in the cooling run at the pressure of 144 MPa.

and the density of the coexisting gas is 3.5 g cm$^{-3}$. When the layer thickness increases, $R_s^2$ first decreases and then increases above 4 nm, while $R_p$ increases monotonically. Therefore we can detect the existence of the wetting layer with high precision by comparing $R_p$ and $R_s^2$.

Figure 4 shows representative results for $R_p$ and $R_s^2$ observed in the cooling run at the pressure of 144 MPa. On the low-temperature side, where bulk mercury is liquid, $R_p$ and $R_s^2$ coincide as expected. On the other hand, at higher temperatures, where bulk mercury is in the gas phase, the relation $R_p = R_s^2$ does not hold, indicating that a thin layer of mercury is formed on the sapphire–mercury interface. When the temperature is decreased in the gas region, both $R_p$ and $R_s$ show a sharp jump, which corresponds to the transition from thin to thick film (the prewetting transition). When the temperature is decreased further, $R_p$ and $R_s$ show another jump, which corresponds to the vapour–liquid transition. In the present work, we assumed that $\tilde{n}_l$ has the same value as that for the bulk liquid mercury. We have roughly estimated that the thickness of the thin layer is about 1 to 2 nm, while that of the thick layer is more than 10 nm. More precise calculation is now in progress.

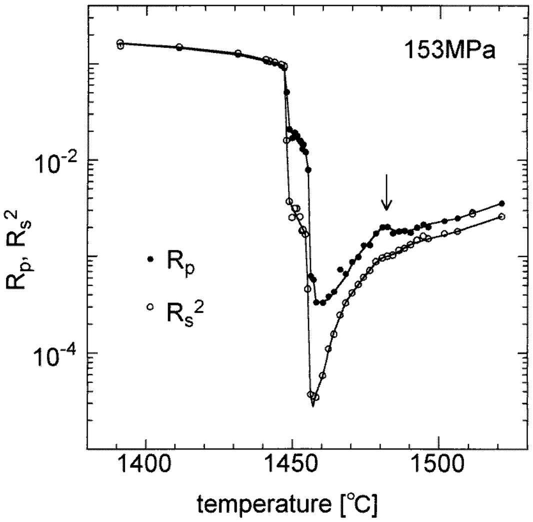

**Figure 5.** Representative results for $R_p$ and $R_s^2$ observed in the cooling run at the pressure of 153 MPa. The arrow indicates the reflectivity anomaly at around 1480 °C.

Figure 5 shows the temperature dependence of $R_p$ and $R_s^2$ at higher pressure (153 MPa). These data were taken in the cooling run. It is noted that there is a reflectivity anomaly at around 1480 °C as indicated by the arrow. $R_p$ reveals a small hump, while $R_s$ shows a small dip. This temperature and pressure correspond to the point where the maximum of the two-dimensional compressibility occurs [2].

## 4. Summary

We have developed a new method for making ellipsometric measurements with 45°-reflection geometry under high temperatures and pressures, and carried out optical reflectivity measurements on fluid mercury against an optically transparent sapphire window at high temperature and pressure up to 1550 °C and 180 MPa. In the 45°-reflection measurements, we used a wedge-shaped sapphire rod, which works as a polarizing prism. By comparing $R_p$ and $R_s^2$, the wetting layer can be detected with high precision, and the occurrence of the prewetting transition was confirmed clearly.

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