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Wetting phenomena of mercury on sapphire studied by optical emissivity measurement

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Abstract. We have carried out simultaneous measurements of the optical reflectivity and the thermal radiation for the mercury–sapphire system. We have found that the optical emissivity shows remarkable changes not only at the liquid–gas transition but also at the prewetting transition of mercury on the sapphire substrate. Furthermore, in the prewetting supercritical phase, a sharp dip in the emissivity is observed, and this anomaly is much stronger than that in the reflectivity. We conclude that this strong anomaly in the emissivity is a clear indication of permittivity fluctuations in the wetting layer, because the emissivity is equal to the 'absorbing power' of the interface (Kirchhoff's law) and it should be sensitive to the diffuse scattering caused by the interfacial fluctuations.

1. Introduction

The prewetting transition is a first-order phase transition between a thin and a thick wetting film on a substrate [1]. A prewetting transition of mercury on sapphire was first evidenced from anomalous behaviours in the optical reflectivity at normal incidence [2], and recently it has been unambiguously confirmed by newly developed ellipsometry [3, 4]. The prewetting line merges tangentially into the bulk liquid–vapour coexistence curve at the prewetting temperature $T_w = 1310\,^\circ\mathrm{C}$, and terminates at the prewetting critical point ($T^c_{pw} = 1468\,^\circ\mathrm{C}$ and $P^c_{pw} = 158.6$ MPa). Anomalies in the optical reflectivity were also observed above T^c_{pw} (i.e. in the prewetting supercritical phase), and they were tentatively interpreted as a phenomenon related to the maximum of two-dimensional compressibility $\chi = \partial\Gamma/\partial\mu$ [2,3], where Γ is the coverage of wetting film and μ is the chemical potential. The density fluctuations in the wetting film are expected to play the major role in this region. A recent Monte Carlo simulation for the Lennard-Jones system supports this interpretation [5], and it is highly desirable to detect directly the interfacial fluctuations by experiment.

In the present work, we have carried out simultaneous measurements of the optical reflectivity and the thermal radiation emitted from a mercury sample behind a sapphire optical window, and found strong anomalies in the emissivity in the prewetting supercritical phase. We discuss the emissivity anomalies in connection with the permittivity fluctuations in the wetting layer.

2. Experimental procedure

Figure 1 shows schematically the experimental set-up for the simultaneous measurement of optical reflectivity at 1064 nm and thermal radiation intensity at 1550 nm. A sapphire rod

6 mm in diameter and 95 mm in axial length was inserted into a molybdenum cell, which was filled with fluid mercury. The cell assembly together with two heaters were set in a steel high-pressure vessel which was pressurized with argon gas. For the reflectivity measurement, a YAG laser (wavelength $\lambda = 1064$ nm) was used as a light source. The light from the laser was chopped at 90 Hz and irradiated into the high-pressure vessel through the sapphire window. The reflected light, together with the thermally radiated light from the mercury–sapphire interface, passed through a band-pass filter, which has one broad transmission band around 1550 nm and two narrow transmission bands at 1346 nm and 1064 nm, and was detected by a GaInAs pin photodiode, which has the maximum sensitivity around 1550 nm. The output signal of the photodiode was separated into a 90 Hz component and a DC component. The former is proportional to the reflectivity at 1064 nm and the latter to the thermal radiation intensity at 1550 nm.

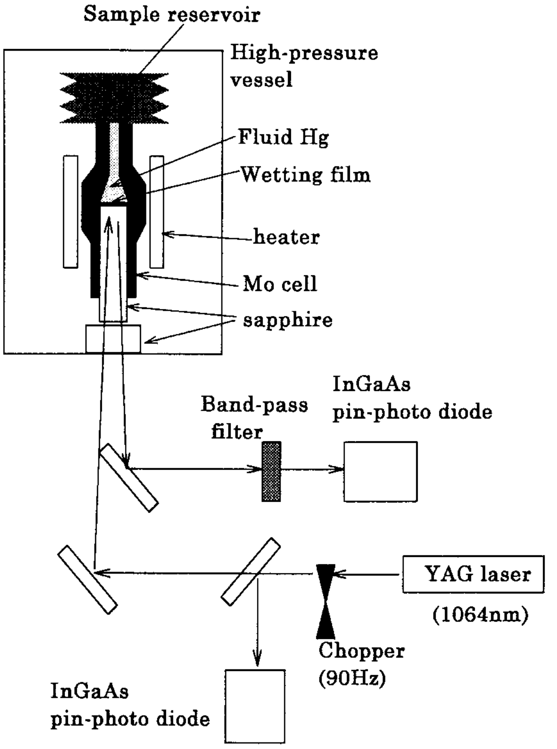

Figure 1. The experimental set-up for simultaneous measurements of the optical reflectivity at 1064 nm and thermal radiation intensity at 1550 nm.

3. Results

We performed the optical measurements at constant temperature T by increasing or decreasing pressure P. Figure 2(a) shows a representative result on the reflectivity and thermal radiation intensity for $T_{\mathrm{w}} < T < T^{\mathrm{c}}_{\mathrm{pw}}$. When the pressure is increased, the reflectivity changes discontinuously at the prewetting transition and the gas–liquid transition, as reported previously [2–4].

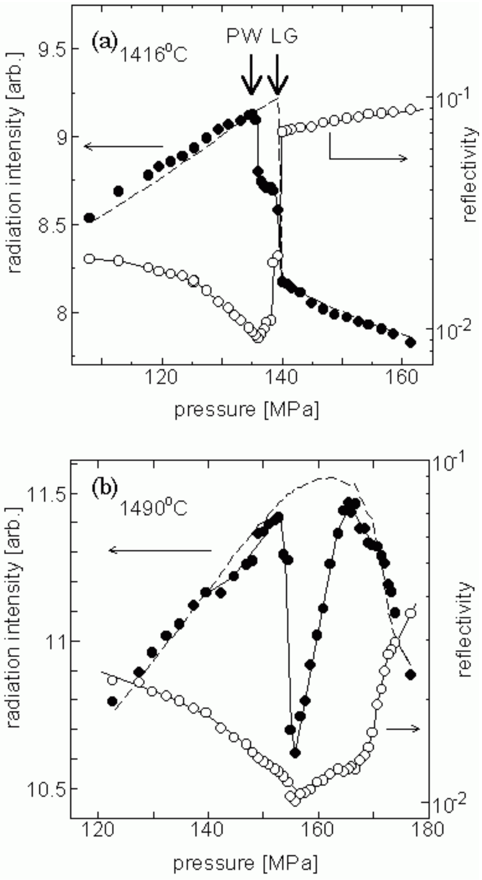

Figure 2. Experimental results at constant temperatures of 1416 °C ($<T^{c}_{pw}$) (a) and 1490 °C ($>T^{c}_{pw}$) (b). The open circles show reflectivity at 1064 nm and the closed circles show thermal radiation intensity at 1550 nm. In (a), the prewetting and liquid–gas transitions are indicated by 'PW' and 'LG', respectively. The dashed lines indicate the calculated I^{tot}_{rad} for the interface between bulk mercury and sapphire. The solid lines are guides for the eyes.

Unlike insulating fluids, the complex refractive index of mercury, $\tilde{n} = n + ik$, changes drastically with density [6, 7]. Therefore the formation of wetting film can clearly be detected from a substantial change of reflectivity [8].

The thermal radiation intensity also shows discontinuous changes at the prewetting transition and the gas–liquid transition points. This result indicate that the wetting phenomena can also be detected by measuring the thermal radiation intensity. It is noticed that these changes in the radiation intensity are nearly opposite to those in the reflectivity.

When the temperature is higher than T^{c}_{pw}, the thermal radiation intensity shows a more striking anomaly. Figure 2(b) shows the experimental results at 1490 °C ($>T^{c}_{pw}$). The reflectivity changes continuously, indicating that the transition from thin to thick film is continuous for $T > T^{c}_{pw}$. On the other hand, the thermal radiation intensity shows a substantial dip around 156 MPa.

In figure 3, the state points where the thermal radiation shows an anomaly are plotted in the P–T phase diagram. We can define the prewetting line and its extension above T^{c}_{pw} from these points, as indicated by thin solid and dashed lines, respectively. The line bends sharply at T^{c}_{pw}.

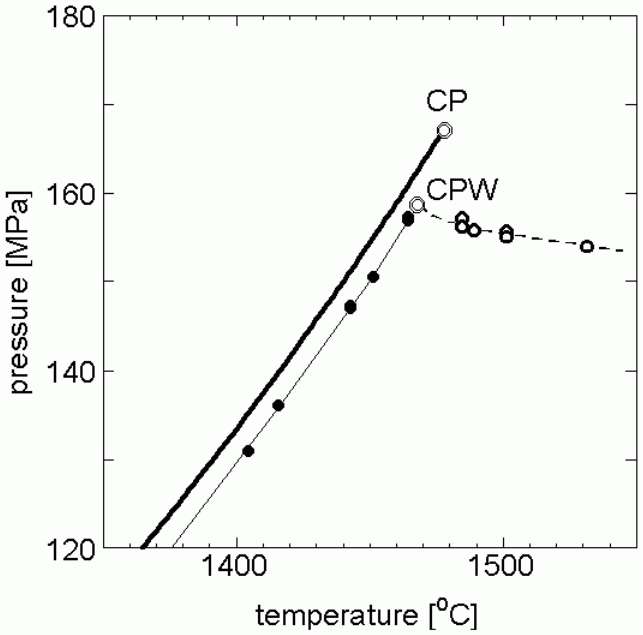

Figure 3. The P–T phase diagram for the mercury–sapphire system. The thick solid line indicates the liquid–vapour coexistence line. The solid circles show the state points where the thermal radiation exhibits discontinuous jumps in the gas region below $T^{\mathrm{c}}_{\mathrm{pw}}$ (see figure 2(a)), and the open circles show the state points where thermal radiation exhibits a minimum above $T^{\mathrm{c}}_{\mathrm{pw}}$ (see figure 2(b)). The thin solid line and dashed line indicate the prewetting line and its extension above $T^{\mathrm{c}}_{\mathrm{pw}}$, respectively.

It should be noted that the dashed line agrees well with the line where the optical reflectivity shows anomalies [2, 3], which were tentatively interpreted as a phenomenon related to the maximum of two-dimensional compressibility.

4. Discussion

The thermal radiation emitted from a surface of some body can be related to its optical properties by using the following equation (Kirchhoff's law) [9]:

$$I_{\mathrm{rad}}(\omega,\theta) = A(\omega,\theta)\cos\theta\, I_{\mathrm{BB}}(\omega). \tag{1}$$

Here we denote the intensity of the radiation with frequency ω from unit surface area at an angle θ to its normal by $I_{\mathrm{rad}}(\omega,\theta)$, and the black-body radiation intensity by $I_{\mathrm{BB}}(\omega)$. $A(\omega,\theta)$ is the 'absorbing power', and is defined as the fraction of light absorbed by the body.

In the present case, 'the body' means the mercury sample behind the sapphire rod, and the surrounding molybdenum cavity. From equation (1), the sapphire rod is not expected to contribute to I_{rad} because it is transparent to the light with the wavelength of 1550 nm. Hereafter, we consider that the absorbing power of the body is equal to that of the fluid mercury and the thin mercury layer in contact with the sapphire surface, because the molybdenum cavity can be considered as a black body. The fraction of light which is *not* absorbed by the body, $1 - A(\omega,\theta)$, consists of a specular reflectivity term $R(\omega,\theta)$ and an off-specular diffuse scattering term due to the interfacial fluctuations [9]. The scattering term should be integrated over the solid angle Ω' into which the light is scattered. Thus I_{rad} can be written as

$$I_{\mathrm{rad}}(\omega,\theta) = I_{\mathrm{BB}}(\omega)\left[(1 - R(\omega,\theta))\cos\theta - \int \mathrm{d}\Omega' \,\frac{1}{A}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'}\right] \tag{2}$$

where $\mathrm{d}\sigma/\mathrm{d}\Omega'$ is the differential cross section of the diffuse scattering and A is an effective surface area of the interface.

Although the emitted light was collimated, we found that the detected radiation has an angular distribution $g(\theta)$ around $\theta = 0°$. By using $g(\theta)$, the total radiation intensity is written as

$$I_{\mathrm{rad}}^{\mathrm{tot}}(\omega) = \int \mathrm{d}\Omega \; g(\theta) I_{\mathrm{rad}}(\theta,\omega) \tag{3}$$

where $\mathrm{d}\Omega = 2\pi\sin\theta\,\mathrm{d}\theta$. We used a Gaussian angular distribution function with the standard deviation $\sigma = 28°$ for $g(\theta)$.

At the pressures and the temperatures far from the liquid–gas coexistence curve where the wetting layer is absent, the observed thermal radiation is well explained by using only the first term in the parentheses of equation (2), corresponding to the bulk specular reflectivity term. The dashed lines in figures 2(a) and 2(b) show the calculated $I_{\mathrm{rad}}^{\mathrm{tot}}$ for the interface between bulk mercury and sapphire.

On the other hand, when the wetting layer is present and the interfacial fluctuations between the layer and the bulk gas are significant, the second term in the parentheses of equation (2), corresponding to the off-specular scattering, should play the major role, especially in the supercritical region.

The discrepancy between the observed $I_{\mathrm{rad}}^{\mathrm{tot}}$ and the dashed lines in figures 2(a) and 2(b) should be attributed to the scattering term.

Within the framework of the modified first Born approximation, the scattering cross section can be expressed in terms of the two-point correlation function of the permittivity fluctuation $\tilde{\epsilon}(\vec{r}, z)$ [10]:

$$\frac{1}{A}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\pi^2}{\lambda^4}\int \mathrm{d}z \int \mathrm{d}z' \; G(\vec{p}, z, z')\left(\sum_{i=1}^{4} f_i^*(z) f_i(z')\right) \tag{4}$$

where

$$G(\vec{p}, z, z') = \int \mathrm{d}^2(\vec{r} - \vec{r}') \;\left\langle \tilde{\epsilon}^*(\vec{r}, z)\tilde{\epsilon}(\vec{r}', z')\right\rangle \exp(\mathrm{i}\vec{p}\cdot(\vec{r} - \vec{r}')) \tag{5}$$

is the Fourier transform of the two-point correlation function along lateral directions $\vec{r} = (x, y)$, and $\vec{p}$ is the momentum transfer parallel to the surface. z is the coordinate normal to the surface, and $z = 0$ at the sapphire substrate. $f_i(z)$ $(i = 1$–$4)$ are functions of the electric field $\vec{E}(z)$, which is modified by the interface, and depend on the incident angle θ and the scattering angle θ' (equations (2.51)–(2.54) of reference [10]).

In order to estimate the interfacial fluctuations, we make the following assumptions. First, we assume that the fluctuations are spatially restricted within the liquid/vapour interface region of the wetting film, i.e. that $l - \Delta l/2 < z < l + \Delta l/2$, where l is the mean thickness of the layer. This assumption is valid when the fluctuation in the permittivity is mainly due to the fluctuation in the film thickness around its mean value l. Second, we assume that the two-point correlation function damps exponentially with distance, and the correlation length is ξ. Then, the two-point correlation function of the permittivity fluctuation can be written as

$$\left\langle \tilde{\epsilon}^*(\vec{r}, z)\tilde{\epsilon}(\vec{r}', z')\right\rangle = \begin{cases} |\Delta\epsilon|^2 \exp(-|\vec{r} - \vec{r}'|/\xi) & \text{for } l - \Delta l/2 < z, z' < l + \Delta l/2 \\ 0 & \text{otherwise.} \end{cases} \tag{6}$$

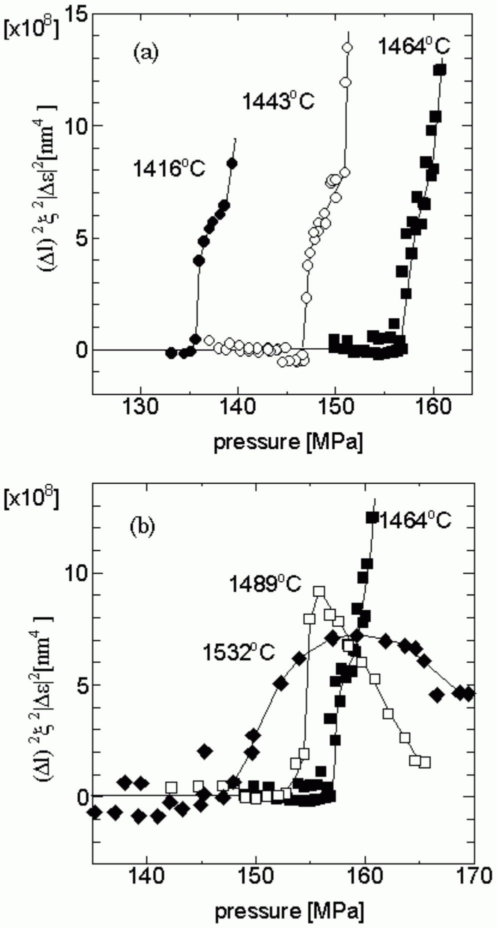

Figure 4. The estimated values of $(\Delta l)^2\xi^2\,|\Delta\epsilon|^2$, which is a measure of the interfacial fluctuation, below $T^{\mathrm{c}}_{\mathrm{pw}}$ (a) and above $T^{\mathrm{c}}_{\mathrm{pw}}$ (b). The solid lines are guides for the eyes.

By Fourier transformation, $G(\vec{p}, z, z')$ can be written as

$$G(\vec{p}, z, z') = \begin{cases} 2\pi\xi^2\,|\Delta\epsilon|^2/(1+\xi^2p^2)^{3/2} & \text{for } l - \Delta l/2 < z, z' < l + \Delta l/2 \\ 0 & \text{otherwise.} \end{cases} \tag{7}$$

ξ and Δl are expected to be much smaller than the wavelength $\lambda = 1550$ nm, because l is estimated to be of the order of tens of nanometres [3, 4], and $\xi \sim l > \Delta l$. In this case, $G(\vec{p}, z, z') \simeq G(0, z, z')$, and the contribution of the permittivity fluctuation to the optical emissivity can be written as

$$-\frac{\pi^2}{\lambda^4}\,2\pi(\Delta l)^2\xi^2\,|\Delta\epsilon|^2\left(\int \mathrm{d}\Omega \int \mathrm{d}\Omega'\, g(\theta)\sum_{i=1}^{4}|f_i(l)|^2\right). \tag{8}$$

Hence, the quantity $(\Delta l)^2\xi^2\,|\Delta\epsilon|^2$, which is a measure of the interfacial fluctuation, can be estimated. Figures 4(a) and 4(b) show the estimated $(\Delta l)^2\xi^2\,|\Delta\epsilon|^2$ below and above $T^{\mathrm{c}}_{\mathrm{pw}}$, respectively. When the temperature is lower than $T^{\mathrm{c}}_{\mathrm{pw}}$, the quantity $(\Delta l)^2\xi^2\,|\Delta\epsilon|^2$ jumps at the prewetting transition, and then diverges when the liquid–gas transition is approached. In the prewetting supercritical region, $(\Delta l)^2\xi^2\,|\Delta\epsilon|^2$ exhibits a peak, which corresponds to the maximum of two-dimensional compressibility. When the temperature is increased, the peak becomes broader.

5. Conclusions

We found that the thermal radiation intensity I_{rad} shows a remarkable change at the prewetting transition. Moreover, in the prewetting supercritical region, we found that I_{rad} exhibits a substantial dip, and this anomaly is much stronger than that in the reflectivity. From Kirchhoff's law, the emissivity is equal to the 'absorbing power' of the interface, and contains information on the reflectivity R and the diffuse scattering cross section $\mathrm{d}\sigma/\mathrm{d}\Omega$ due to the interfacial fluctuation. The strong anomaly in the emissivity in the prewetting supercritical phase is a clear indication that there exist permittivity fluctuations in the wetting layer. The scattering cross section can be expressed in terms of the two-point correlation function of the permittivity fluctuation, and the quantity $(\Delta l)^2\xi^2\,|\Delta\epsilon|^2$, which is a measure of the interfacial fluctuation, was estimated.

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References

[1] Dietrich S 1988 *Phase Transitions and Critical Phenomena* ed C Domb and J Lebowitz (New York: Academic) p 1
[2] Yao M and Hensel F 1996 *J. Phys.: Condens. Matter* **8** 9547
Hensel F and Yao M 1997 *Eur. J. Solid State Inorg. Chem.* **34** 861
[3] Ohmasa Y, Kajihara Y and Yao M 1998 *J. Phys.: Condens. Matter* **10** 11 589
[4] Ohmasa Y, Kajihara Y Kohno H, Hiejima Y and Yao M 1999 *J. Non-Cryst. Solids* **250–252** 209
[5] Omata K and Yonezawa F 1998 *J. Phys.: Condens. Matter* **10** 9431
[6] Ikezi H, Schwarzenegger K, Simons A L, Passner A L and McCall S L 1978 *Phys. Rev.* B **18** 2494
[7] Hefner W, Schmutzler R W and Hensel F 1980 *J. Physique Coll.* **41** C8 62
[8] Berning H P 1963 *Physical Properties of Thin Films* vol 1, ed G Hass (New York: Academic)
[9] Planck M 1914 *The Theory of Heat Radiation* Part I (Blakiston) ch II
Landau L D and Lifshitz E M 1958 *Statistical Physics* (New York: Pergamon) ch V, § 60
[10] Dietrich S and Haase A 1995 *Phys. Rep.* **260** 1