

# Triple-Point Wetting of Molecular Hydrogen on Tailored Substrates

Masoud Sohaili, Jürgen Klier, and Paul Leiderer

Fakultät für Physik, Universität Konstanz,  
Postfach 5560 M676, D-78434 Konstanz, Germany

*Triple-point wetting is a well-known phenomenon of many simple adsorbates on solid substrates. It implies that in the liquid phase above the triple-point temperature,  $T_3$ , complete wetting with the formation of arbitrarily thick films is observed, whereas below  $T_3$  only a few monolayers of the solid phase are adsorbed at saturated vapour pressure. This effect is usually ascribed to substrate-induced strain in the solid film, which occurs due to lattice mismatch and/or the strong van der Waals pressure in the first monolayers. Molecular hydrogen is a suitable system to investigate this phenomenon, in particular by tailoring the adsorbate-substrate interaction by means of thin preplating layers of other adsorbates, and by introducing disorder into the system by using not only the pure systems  $H_2$  and  $D_2$ , but also mixtures thereof. In particular the dependence of  $T_3$  of the mixture on the mass ratio of its components is measured and deviations from the simple van der Waals law are discussed. The experiments show that triple-point wetting is a rather dominating effect, which in contrast to expectation persists even if the system parameters are widely varied, indicating that the present picture of this effect is incomplete.*

*PACS numbers: 67.70.+n, 68.45.Da, 68.45.Gd.*

## 1. INTRODUCTION

Physisorbed films of solid molecular hydrogen are of practical importance for various applications<sup>1</sup>. However, the preparation of films thicker than a few monolayers (ML) is not possible in thermodynamic equilibrium due to the fact that solid hydrogen on most substrates exhibits incomplete wetting (i.e. Stranski-Krastanov growth). So in order to form a thick hydrogen film the molecules have to be quench-condensed (a nonequilibrium

situation). Annealing these films, however, leaves big crystallites connected by a very thin film of typically 3 ML on the substrate <sup>2</sup>.

We report on the dependence of the triple-point and wetting behaviour of D<sub>2</sub>-preplated H<sub>2</sub> films as well as H<sub>2</sub>-D<sub>2</sub> mixture films with two different molecular concentrations adsorbed on differently prepared gold substrates.

D<sub>2</sub> is used as a preplating material to investigate the adsorption behaviour of pure H<sub>2</sub> on Au. This is motivated by the idea of tuning the adsorbate-substrate interaction (between H<sub>2</sub> and Au) and so to influence the nonwetting behaviour of hydrogen molecules. According to a theory by Gittes and Schick <sup>3</sup> one should expect that this scenario can be changed to complete wetting of the solid phase under equilibrium conditions, if the interaction with the substrate is modified: On conventional substrates the interaction is so strong that induced strain in the adsorbed film prevents complete wetting; reducing this interaction, e.g. by preplating with a proper material, should reduce the strain and lead to complete wetting, thus allowing to grow thick epitaxial hydrogen layers.

In this paper we show that using D<sub>2</sub> as a preplating material influences the van der Waals interaction of the H<sub>2</sub> molecules to the Au substrate, but still the hydrogen does not wet the Au below T<sub>3</sub>. Diluting molecular hydrogen by D<sub>2</sub> is found to affect its bulk triple-point, which can be varied from T<sub>3</sub> ≈ 14 K in case of pure H<sub>2</sub> to T<sub>3</sub> ≈ 19 K for pure D<sub>2</sub>, with a roughly linear dependence on concentration. Hints for a possible isotopic separation of the H<sub>2</sub>-D<sub>2</sub> solutions are not found in our measurements <sup>4,5</sup>.

## 2. EXPERIMENTAL PROCEDURE

All the experiments were performed by exciting surface plasmons (SP) at the interface of a gold film and the adsorbed material. The Au films, of a thickness of 45 ± 5 nm (this thickness provides an optimum in SP resonance), were usually prepared by conventional thermal evaporation onto a glass prism in a high vacuum chamber. Then the Au-evaporated prisms were mounted in a Cu cell, which was placed into a small optical <sup>4</sup>He flow cryostat. After reaching high vacuum the cell was cooled to the experimental temperatures. In some runs the Au-films were heated during cool-down in order to reduce contamination of the surface by condensation of the residual gas left in the cell. The temperature was varied between 7 and 30 K and controlled to about 1 mK. Using the SP spectroscopy method <sup>2,6</sup> gave a resolution of the thickness of the adsorbed films of ≈ 0.1 ML.

The adsorbed films were prepared above the triple-point temperature by carrying out adsorption isotherms up to the saturated vapour pressure,

$P_0$ , so to have always a thick equilibrated wetted liquid film. Then the temperature was slowly swept substantially below  $T_3$ , and back again (i.e. doing cooling and warming scans). Before taking each data point enough time was given to ensure thermodynamic equilibrium. The equilibration times were found to differ a lot depending on the thickness of the adsorbed film and the temperature region.

### 3. RESULTS

For  $H_2$  on bare Au surfaces the phenomenon of triple-point dewetting, i.e. incomplete wetting below  $T_3$ , is well established<sup>8</sup>. Above  $T_3$  the liquid phase completely wets the surface. One observes a fast, nearly step-like growth, of the  $H_2$  thickness,  $d$ , at low  $P/P_0$ . Hereby the first few monolayers usually solidify due to the strong van der Waals interaction to the substrate. After adding more  $H_2$  to the cell the growth of the film thickness above  $T_3$  resembles the typical Frankel-Halsey-Hill behaviour, i.e.,  $d^{-3} \propto \ln(P/P_0)$ . Approaching  $P/P_0 = 1$  the film thickness diverges. Below  $T_3$ , however, the film thickness remains finite at  $P/P_0 = 1$ .

In order to suppress triple-point dewetting we have tried to manipulate the substrate strength between  $H_2$  and Au via preplating the Au film. In our earlier studies we have preplated the Au films with Ne, Ar, or  $CH_4$ . However the experiments showed that for all combinations of preplated material the equilibrium  $H_2$  film thickness is – apart from small differences – the same as without preplating<sup>6</sup>.

In the studies here we have done preplating with  $D_2$ . This was achieved by taking an adsorption isotherm of  $D_2$  at 20 K when the  $D_2$  molecules are in the liquid state (c.f.  $T_3$  for pure  $D_2$  is 18.93 K). Having established saturated vapour pressure we cooled down to 10 K. As can be seen from Figs. 1 and 2 also  $D_2$  on Au shows triple-point dewetting. At  $T \ll T_3$  the preplated thickness of the  $D_2$  is about 3 ML<sup>7</sup>, quite similar to  $H_2$ . After warming up to 15 K we have taken a  $H_2$  adsorption isotherm until reaching saturated vapour pressure of  $H_2$ . At saturation there are a few ten MLs of liquid  $H_2$  on top of the preplated solid layers of  $D_2$  on Au. Then the cell is cooled down to 7 K and the typical dewetting behaviour is observed<sup>6</sup>, see Fig. 1. However, this time there was no distinct change at the expected triple-point of pure  $H_2$ ,  $T_3(H_2) = 13.9$  K but only the usual decrease in film thickness.

Warming up to 15 K shows a small change in the dependence of the  $H_2$  thickness on temperature, hereby a hysteresis develops for  $T > 13$  K, which increases as the temperature increases. This indicates that there is some partial mixing between the  $H_2$  and  $D_2$  molecules which shifts a possible

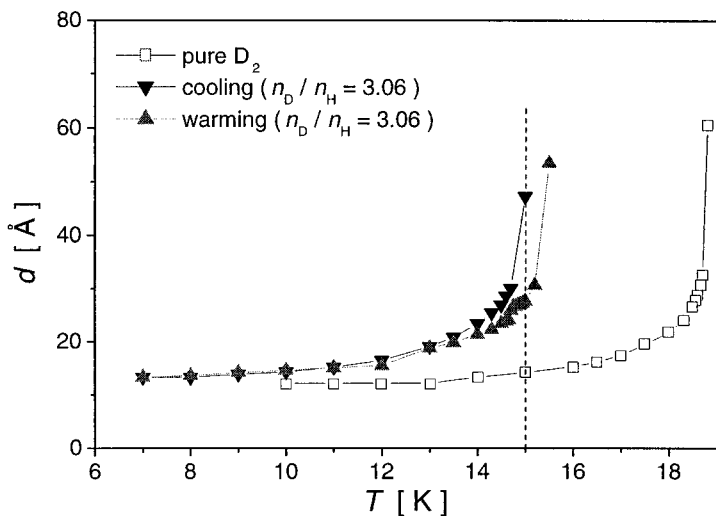


Fig. 1. Shown is the total adsorbed film thickness of H<sub>2</sub> and D<sub>2</sub> as function of temperature (cooling (▼) and warming (▲)) on a D<sub>2</sub> preplated Au surface. The dashed line indicates the temperature at which H<sub>2</sub> was added to the cell. (□) show the  $T$ -dependence of the adsorbed film of preplated D<sub>2</sub>.

existing dewetting-point to higher temperatures.

In order to establish a complete mixing of H<sub>2</sub> and D<sub>2</sub> we warmed the cell up to about 30 K. At this temperature both components are in their gas phases which should ensure a good mixing. After leaving the system at this temperature for several hours we slowly cooled down the cell to study the dewetting and to map out a possible *effective* triple-point of the mixture. As one can see from Fig. 2 there is a dewetting behaviour similar to pure H<sub>2</sub> or D<sub>2</sub>, but with a shifted triple-point where  $T_3(\text{H}_2) < T_3(\text{mixture}) < T_3(\text{D}_2)$ .

After warming up the cryostat to room temperature and thoroughly pumping the cell, we have repeated the above procedure, however, this time with a different concentration of H<sub>2</sub> in D<sub>2</sub>. To establish this variation in concentration we just condensed in more H<sub>2</sub>, after reaching  $P_0(\text{H}_2)$ , during the adsorption isotherms.

The dependence of the film thickness on temperature for the two different concentrations of D<sub>2</sub> in H<sub>2</sub>, as well as for the pure D<sub>2</sub> and pure H<sub>2</sub> case, is shown in Fig. 2. The result indicates an approximately linear dependence of the *effective* bulk mixture triple-point temperature on concentration, see

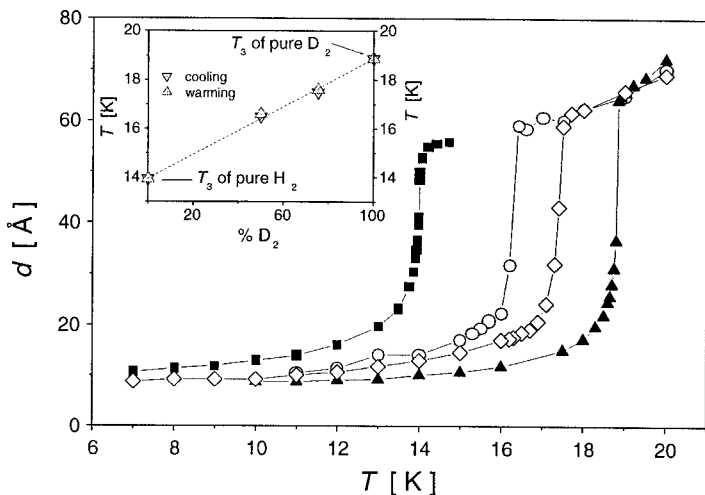


Fig. 2. Shown is the adsorbed film thickness for pure  $\text{H}_2$  and  $\text{D}_2$  and  $\text{H}_2$ - $\text{D}_2$  mixtures as function of temperature (warming-up curves). ( $\circ$ ) are for  $n_D/n_H = 1.0$ , ( $\blacksquare$ ) for pure  $\text{H}_2$ , ( $\blacktriangle$ ) for pure  $\text{D}_2$ , and ( $\diamond$ ) for  $n_D/n_H = 3.06$ . The drastic increases of the film thickness pinpoint  $T_3$ , which is  $(16.4 \pm 0.01)$  K for  $n_D/n_H = 1.0$  and  $(17.5 \pm 0.01)$  K for  $n_D/n_H = 3.06$ . The uncertainty in the absolute thickness is less than 1 ML. Inset: shown is the dependence of the effective  $T_3$  on the concentration of  $\text{D}_2$ .

inset in Fig. 2. But using these mixtures does not alter the dewetting behaviour below  $T_3$ . However, in the region of  $T_3$  there is pronounced hysteresis between cooling and warming (not shown in Fig. 2). This behaviour is not observed for the pure isotopes. A detailed analysis of this behaviour will be presented elsewhere.

Apparently also preplating with  $\text{D}_2$  does not qualitatively change the usual triple-point dewetting (Fig. 1), and even for  $\text{H}_2$ - $\text{D}_2$  mixtures the same phenomenon is observed. There may be other reasons for the incomplete wetting below  $T_3$ . Therefore we have investigated what happens if a) the contamination of the surface is reduced, and b) if the roughness is reduced.

a) Contamination of the surface occurs either during preparation of the cell setup or during cooling down (although the cell is pumped to high vacuum conditions). Therefore we did laser heating of the surface under study during cooling from room temperature till reaching about 50 K. However, no difference in the wetting behaviour was observed, neither for the adsorption

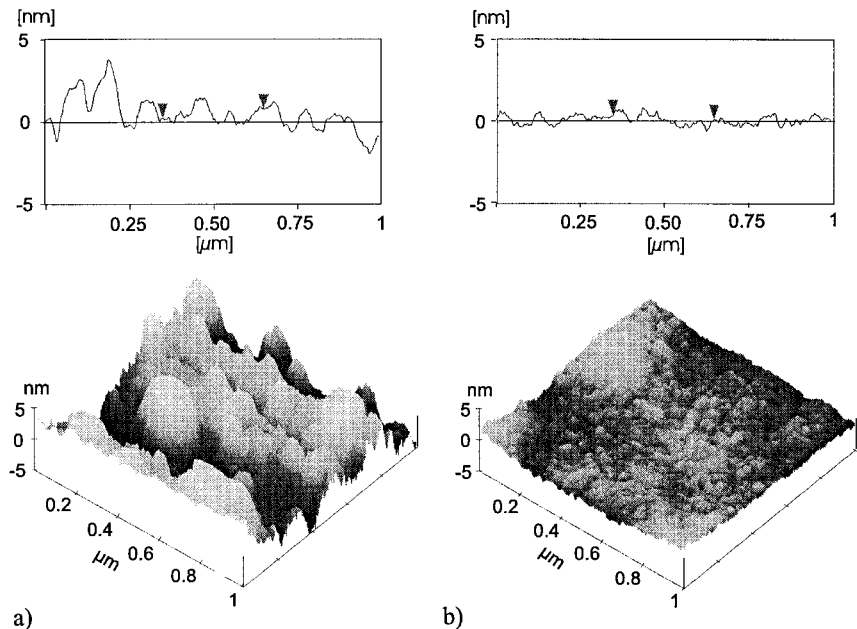


Fig. 3. a) A typical  $1000 \text{ nm} \times 1000 \text{ nm} \times 10 \text{ nm}$  atomic force microscope (AFM) image of a Au film evaporated at room temperature on a glass prism; the top shows a line scan of this image. b) With the same resolution generated AFM-image of Au, however this time initially thermal evaporated onto a Si-wafer, see text. A typical line scan is shown again on the top.

isotherms nor for the temperature scans between the heated and not heated Au surfaces. Perhaps our process of cleaning the surface was not complete, but at least we should have got rid of most possible contaminants like water.

b) Hence the important factor causing triple-point dewetting might be the roughness of the substrate<sup>11</sup>. Therefore we have analyzed some of our Au surfaces with an atomic force microscope and found that, although all surfaces look smooth on an optical scale, they are quite rough on a more microscopic scale, see Fig. 3a. This is well-known and can be understood on how these surfaces are prepared – the thermal evaporation produces a quench-condensed Au film which is usually rough<sup>12</sup>. Therefore we tried to create a smoother Au surface. For that we have evaporated Au on a Si-wafer. Then we glued this wafer with the Au-side onto a glass prism. After the glue had dried we carefully removed the wafer. The result is shown in Fig. 3b. The surface of the Au is much smoother compared to the standard

prepared Au film, as it resembles now the interface to the Si-wafer. In spite of the reduced roughness of such a surface the measured thickness of H<sub>2</sub> or D<sub>2</sub>, however, was the same.

#### 4. CONCLUSIONS

We have investigated the triple-point dewetting behaviour of pure H<sub>2</sub>, D<sub>2</sub>, and H<sub>2</sub>-D<sub>2</sub> mixture films, adsorbed under equilibrium conditions on various Au surfaces. In order to suppress the dewetting behaviour below  $T_3$  we have preplated the Au surfaces to reduce the high substrate strength between H<sub>2</sub> and Au and so, according to theory<sup>3</sup>, achieve complete wetting of H<sub>2</sub> in the solid phase. However, in all preplating cases we observed dewetting below  $T_3$ . Also modifying the Au surface in order to reduce contaminants and surface roughness did not influence the dewetting behaviour.

We have also investigated H<sub>2</sub>-D<sub>2</sub> mixtures and found the same dewetting behaviour below the triple-point. No sign of phase separation within the measured temperature range was observed and the observed effective  $T_3$  of the mixtures showed a nearly linear dependence on concentration.

#### ACKNOWLEDGMENTS

This work is supported by the Deutsche Forschungsgemeinschaft under grant Le 315/20-1 within the Priority Program 'Wetting and Structure Formation at Interfaces'.

#### REFERENCES

1. U. Albrecht *et al.*, *J. Low Temp. Phys.* **22**, 117 (1996).
2. U. Albrecht *et al.*, *Surf. Sci.* **283**, 419 (1993).
3. F.T. Gittes and M. Schick, *Phys. Rev. B* **30**, 209 (1984).
4. S.N. Ishmaev *et al.*, *JETP* **75**, 382 (1992).
5. M. Bienfait *et al.*, *Phys. Rev. B* **60**, 11773 (1999).
6. J. Klier, C. Weichhard, and P. Leiderer, *Physica B* **284**, 391 (2000).
7. During cooling the D<sub>2</sub> (or H<sub>2</sub>) leaves the Au surface via the vapour phase and adds to the bulk at the bottom of the cell.
8. see, e.g., ref. 1 and refs. cited therein.
9. J. Krim, J.G. Dash, and J. Suzanne, *Phys. Rev. Lett.* **52**, 640 (1984).
10. G. Vidali *et al.*, *Surf. Sci. Rep.* **12**, 133 (1991).
11. L. Fleischmann *et al.*, *J. Low Temp. Phys.* **119**, 615 (2000).
12. K.H. Müller, *Surf. Sci.* **184**, 375 (1987).