Wetting Studies of Solid and Liquid Hydrogen Isotope Films

DISSERTATION

zur Erlangung des akademischen Grades des Doktors der Naturwissenschaften (Dr. rer. nat.) an der Universität Konstanz Fachbereich Physik

vorgelegt von

Masoud Sohaili

Konstanz, Juni 2004

Tag der mündlichen Prüfung: 29. Juli 2004

Referent: Prof. Dr. Paul Leiderer, Universität Konstanz
Referent: Prof. Dr. Hartmut Löwen, Heinrich-Heine-Universität
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Introduction

Thin liquid films on solid substrates are present in everyday life, e.g., as a lubricant film on the cornea of our eyes or on the pistons in a car’s engine, but also as ink on a transparency. In some cases, these films are not stable on their substrates and bead up. This is a phenomenon that is easily observable if one tries to paint an oily surface. Therefore, any paint or glue usually comes with instructions to thoroughly clean oil and dust off the surface to be coated or glued, otherwise the liquid layer will not be stable and will bead up. In the ideal case, a droplet of the coating liquid spreads spontaneously on the surface. However, a layer of oil or dust usually prevents wetting and the coating may dewet.

Wetting behaviour is always interesting when the properties of the interfaces become important. Interface properties have an effect on the adhesion of lacquers and lubricants to the surfaces, coating of optical glasses, capturing photographic emulsions or preventing surface corrosion. For example a hole in a lacquer film, even smaller than 1 mm$^2$, can cause a big damage in the body paint of a car.

In this work the more fundamental aspects of the wetting phenomena are considered. Often, this concerns the wetting of simple systems like hydrogen or noble gases on solid substrates. In recent years, much effort has been put into the understanding of dewetting phenomena in physisorbed films on solid substrates, both experimentally [You90, You93, Hes91, Mig86, Rie97, Mis99, Kri84, Bru00, Wu98, Mig88, Lei92, Alb93a, Alb93b, Alb96, Kli00, Soh01, Tib03] and theoretically [Das81, Pan82, Hus84, Git84, Pan83]. In addition, a number of reviews exists which cover almost all important theoretical aspects of the field, like those by Dietrich [Die88] and Schick [Sch90].

From a fundamental point of view the growth of multilayer films on an attractive substrate can be divided into two groups. The first is called complete-wetting when the thickness of the film increases with increasing vapour pressure, and diverges as the vapor pressure approaches the saturated value. In incomplete- or partial-wetting, the thickness of the film remains finite at the bulk coexistence. For a given adsorbate and substrate combination a transition may occur from incomplete to complete wetting as a function of temperature [Pan82].

Such a behaviour has already been observed for many physisorbed systems in which the thickness of the adsorbed film increases from an incomplete-wetting (thin) solid film into a complete-wetting (thick) liquid film at its bulk triple-point, $T_3$ [Kri84]. Theoretically, the lattice mismatch between the film and the substrate is considered to be responsible for the finite thickness of the solid film [Hus84, Git84]. There is a large number of measurements which are devoted to adsorption isotherms of rare gases on graphite [You90, You93, Hes91], silver [Mig86], magnesium oxide [Rie97], carbon dioxide [Mis99], and gold [Kri84, Bru00] mostly in the thickness range of one to ten monolayers.

Multilayer hydrogen films have been studied on graphite substrates via volumetric adsorption isotherms [Dau81] and ellipsometry [Wu98] or on silver via quartz-crystal microbalance [Mig88]. Intensive investigations of hydrogen on gold and preplated gold substrates have been the subject of a series of experiments [Lei92, Alb96, Kli00] in which the surface plasmon spectroscopy technique
was used. Films of mixtures of hydrogen-deuterium [Soh01, Tib03], and thick quench-condensed films [Alb93a, Alb93b, Fle00b, Fle00a] have been investigated via this method. Only a few measurements on the surface of silicon have been reported [Ang03, Kli86].

The main goal of this work has been to investigate the behaviour of solid hydrogen films on the substrates with different surface profiles. Moreover, in addition to the lattice mismatch effects mentioned above [Esz02] there are hints that strain in the solid films, induced by the finite roughness of the substrate, is important for triple-point dewetting.

Thick solid films of hydrogen isotopes have subtle fundamental applications and it is, therefore, important, from a practical point of view, to understand the incomplete wetting of these films below the triple-point of the respective adsorbate. Solid hydrogen films can be used as a substrate [Kon91a, Kon91b, Mon93] to hold electrons at a distance above them in experiments on surface state electrons. Preparation of thick solid tritium films play a decisive role in experiments designed to measure the neutrino rest mass [Ott94, Ott95, Bac94]. Solid deuterium films are necessary in nuclear fusion [Dav83, Cra86]. Moreover, hydrogen films, which have a quantum nature due to their light molecular mass, offer another system for studying relationships which may exist between the quantum nature of a system and its wetting properties. For example, hydrogen superfluidity on relatively thick solid layers of hydrogen has been predicted [Wag94, Wag96].

The outline of this work is as follows:

In chapter 1 the properties of the physisorbed films are introduced from a more phenomenological point of view. This is done by introducing the interaction forces among atomic size particles and between the particle and the solid wall. The growth of a physisorbed film in the vicinity of such surfaces, often in the early stages of the growth, is described. The deviations from the predicted phenomenological behaviour are discussed. In the end, some experimental methods related to this subject are introduced.

In chapter 2 wetting transitions and other related phenomena are discussed. Wetting phenomenon is introduced by considering the simple case of a drop (liquid) on the surface of a solid substrate. Thereafter an overview is given on the theoretically predicted and experimentally observed wetting phenomena in physisorption systems. It is emphasized that for the majority of the physisorption systems triple-point wetting takes place. Some exceptional cases are mentioned at the end of the chapter.

In chapter 3 the reasons for the dewetting of substrates by solid adsorbates are explained. This is done from a microscopic point of view. It is shown that the role of the surface qualities of the substrate on the wetting behaviour of the adsorbate must be taken into account.

In chapter 4 the surface plasmon spectroscopy and ellipsometry which are widely used in the measurements of the present work are introduced. In addition, determination of the thickness of the adsorbed film from the measured optical parameters of the surface by these methods is discussed.

In chapter 5 the constructions of our experimental setups are shown. The details of each of the experimental setups are given and the functions of the main optical components of the setups are briefly described.

In chapter 6 the main achievements of this work that include the investigations on gold substrates by surface plasmon spectroscopy and on silicon by using ellipsometry are noticed and discussed. The recent results of laser annealing and cleaning are represented.
Chapter 7 points out the future research activities which may be done based on the achievements obtained here.
Parts of this work have been already published in the following articles

M. Sohaili, J. Klier, P. Leiderer,
Triple-Point Wetting of Molecular Hydrogen on Tailored Substrates,

A. Esztermann, M. Heni, H. Löwen, J. Klier, M. Sohaili, P. Leiderer,
Triple-Point Wetting of Rough Substrates,

J. Angrik, M. Sohaili, J. Klier, P. Leiderer,
The effect of the roughness on the $T_3$-dewetting of molecular hydrogen,

S. Tibus, M. Sohaili, J. Klier, P. Leiderer,
Influence of the concentration of H$_2$-D$_2$ mixtures on their triple-point dewetting behaviour,

M. Sohaili, J. Klier, P. Leiderer,
Triple-Point Wetting of Molecular Hydrogen Isotopes,
1 Phenomenology of Physisorption Films

In this chapter, physisorption films will be introduced. The interaction aspects between the atoms in such films will be taken into consideration. It will be shown that the behaviour of such films can, in general, be explained by some theoretical formulations. The important theoretical basis are briefly noted but the details of them are referred to the cited literature. A step-like structure of the growth can be seen in the 2-dimensional growing mode. But as the film grows and at higher temperature this structure smears out which shows a continues growth at upper layers or higher thicknesses. Under experimental conditions there are some deviations from the theoretical predicted behaviour which are discussed. At the end the experimental methods together with their abilities used in physisorption measurements are noted.

1.1 Physisorption

Physisorption means that the adsorbed atoms or molecules\(^1\), in contrast to chemisorption, will make no chemical bonds to the substrate. But they are bounded to the substrate only through the van der Waals\textsuperscript{(vdW)} interaction. That means the electronic structure of the adsorbate and the substrate remains unchanged. Considering the order of magnitude of a typical potential depth, a few K to 100 K \cite{Vid91} depending on the system, one realizes that this can be done by sufficient lowering the temperature such that the thermal excitations become small compared to the potential depth of the substrate.

1.2 Van der Waals Interaction

The vdW-interaction results from the electrostatic interaction of two induced-dipoles which exists between all polarizable particles. This is a pure quantum mechanical phenomenon which is investigated using the perturbation theory of London \cite{Lon37}. Accordingly, the interaction potential \(V\) between two particles separated by a distance \(r\) from each other behaves as \(r^{-6}\). At large distances (above 100 Å), where the finite expansion velocity of electromagnetic waves becomes significant, there exists retardation in the dipole-dipole interaction which yields an asymptotic behaviour \(r^{-7}\). At very short distances atom or rather molecule orbitals overlap. This causes an extreme repulsion of the nuclei. Often, this is taken into account by including a term \(r^{-12}\) in the phenomenological Lennard-Jones(LJ) potential. Therefore for spherical and isotropic interacting particles the LJ-potential, in the nonretarded regime, can be approximated as

\[
\phi(r) = 4\epsilon\left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6\right]
\]

\(1\)In general, a stable electronic structure is meant since otherwise chemisorption may take place.
where $\varepsilon$ and $\zeta$ (see Fig. 1.1) are the potential strength and the particle diameter, respectively. Experimentally measured interaction potentials of noble gases often show a steeper behaviour in the region of the short range repulsion. This is considered in a so-called Aziz-potential [Azi84]. The LJ-Parameters of different materials can be found in [Col83].

Figure 1.1: Lennard-Jones potential between two atoms separated by a distance $r$ from each other. One of the atoms is taken to be at $r = 0$. The equilibrium position for the other will be at $r = \zeta$. Below this value a high repulsion, which prevents the overlapping of the two atoms nuclei, will occur.

In the case of an adsorbate atom at a distance $z$ from a surface, the proper interacting potential can be obtained by summing over all pairwise LJ-interactions of the adsorbate with the substrate atoms filling the half space, i.e., $0 < z < \infty$. The final result of this calculation (see, e.g., [Che93a]) reads

$$\phi(z) = \frac{4C_3^3}{27D^2z^9} - \frac{C_3}{z^3}$$  \hspace{1cm} (1.2)

where $C_3$ and $D$ are the vdW-coefficient and the potential depth, respectively. At large enough distances, the contribution of the first term is negligible, that means the potential behaves as $z^{-3}$ (in retardation regimes as $z^{-4}$) [Das80].

### 1.3 Van der Waals Films

Now we consider a gas of atoms near a surface. The interaction with the substrate reduces the free energy of the gas, as a result, in thermodynamic equilibrium, the gas density increases in the vicinity of the substrate. Accordingly, a thin film of thickness $d$ will grow close to the saturated vapor pressure. The thickness $d$, which is a result of the vdW-interaction potential, is now determined by the equilibration of the vdW-potential with the chemical potential-difference of the film and the gas, i.e.,

$$k_B T \ln \frac{P_0}{P} = \frac{\alpha}{d^3}$$  \hspace{1cm} (1.3)

where $P$ and $T$ are pressure and temperature, respectively. $P_0(T)$ is the saturated vapour pressure of the adsorbate at temperature $T$ and $\alpha$ is the Hamaker-constant [Ham37] which can be determined
from the electronic properties of the adsorbate and the substrate [Bru83, Rau82, Vid81, Col83].

Often $\alpha$ deviates from experimental results. This is a direct consequence of the assumption which relies on the pairwise-additivity nature of vDW-interaction. This discrepancy can be avoided by using fundamental theories of Lifshitz et al. [Lif56] and Dzyaloshinskii et al. [Dzy60], such as the calculation of Rauber et al. [Rau82] and Cheng et al. [Che88]. A detailed information on the interaction of physisorbed films can be found in the book of Israelachvili [Isr92].

The adsorption isotherms which are explained by Eq. 1.3 are named, after Frenkel-Halsey-Hill [Fre49, Hal48, Hil49], who initially and independently described this relationship, as FHH-adsorption isotherm. Fig. 1.2 illustrates a typical adsorption isotherm of argon on gold prepared on a smooth quartz crystal. The resulting film thickness is plotted as a function of reduced pressure $P/P_0$.

It may be noted that there are some more phenomenological descriptions of adsorption behaviours such as Langmuir-isotherms of Langmuir [Lan18] and BET-isotherms from Brunauer, Emmett and Teller [Bru38]. We consider the FHH, since it is a direct consequence of the interaction between adsorbate and substrate.

### 1.4 Adsorption in 2-Dimension

In this section we introduce briefly the adsorption growth at its very early stages. That is where the layering growth takes place. This is often reminiscence of a 2D growth.

A deeper insight into the growth of physisorbed films shows a stepwise or layering growth, which is experimentally confirmed by detecting monolayer steps in the adsorption isotherm [Wu98, Ham83]. Theoretically, this behaviour can be described again by rewriting Eq. 1.3 in the form of

$$k_B T \ln P_0/P_i = \frac{\alpha}{d_i^3}$$

(1.4)

---

2 Strictly speaking, $\alpha = \alpha_{AA} - \alpha_{AS}$, where $\alpha_{AA}$ and $\alpha_{AS}$ are the Hamaker-constants of adsorbate-adsorbate and adsorbate-substrate, respectively. In addition $\alpha$ and $C_3$, vDW-constant, are related to each other through $\alpha = -\frac{3}{8} C_3 \rho$, where $\rho$ is the density.
Figure 1.3: Set of adsorption isotherms of HD on highly oriented pyrolytic graphite (HOPG) at selected temperatures, labeled on the left. A range of reduced pressure, 0.5-0.95, including the fourth, fifth and sixth steps is shown. The steps in the adsorption isotherms smear out as the temperature increases. [Wu98].

1.5 Deviations from FHH-Model

In the following we briefly introduce some aspects of the deviations from the FHH-behaviour. These include the effects of thermal fluctuations and the substrate heterogeneity, both of which cause the film thickness to increase in the intermediate range of an adsorption isotherm.

As pointed out in section 1.3, we are interested in knowing whether an adsorption isotherm can be fully explained using Eq. 1.3 of FHH. Although this simple theory is expected to hold on thick films, often there are discrepancies between the experimental results and the theoretical predictions (see Panella et al. [Pan96] for an overview). At first glance, it seems that some other effects should be
1 Phenomenology of Physisorption Films

Figure 1.4: Plotted is the chemical potential (relative to the bulk) vs coverage of methane on graphite at temperature between 80 and 96 K. The process of the first monolayers is shown by measuring the heat-capacity and vapor pressure in a calorimetric cryostat (see also Fig. 1.3). In principal, whenever the isotherms coincide then the film behaves like a slab of bulk. This shows again the transition from a structured to a continuous growth as the temperature of the adsorption increases [Ham83].

...taken into account to be able to explain the discrepancies. One conjecture would be whether there are some other interactions which play a role in the adsorption behaviour. Such interactions are already observed for systems like water on silver [Pan96] or alkane on gold [Bra93]. On the other hand, FHH-theory always neglects the possible phase changes during the adsorption of film (indeed FHH is adequate for explaining the growth of liquid films near saturated vapor pressure).

This can be explained by taking the note that for an adsorbate on a substrate the strength of interaction is greater for the layers in the vicinity of the substrate than for the upper layers of the film. It has been shown by different authors [Mig86, Mig88, Zhu88, Kri85, Pet89a] that for the first few monolayers, which strongly interact with the substrate underneath, freezing occurs. That is, the first few monolayers are solid even at some temperatures above the bulk melting point of the adsorbate.

1.5.1 Fluctuations

Mecke et al. [Mec96] have treated this problem more quantitatively by including the effect of thermally excited fluctuations in the film. That means the dynamical processes in equilibrium can also change the adsorption properties of thin films. In their model, there is an extra contribution to the chemical potential of the film which results from thermal fluctuations. As a result the overall thickness increases, in particular, in the middle stages of the adsorption isotherm. The agreement of the theory with the experimental data is very good [Vor01, Vor97]. Fig. 1.5 shows the results of this theory (solid line) with those of FHH (dashed line). The solid squares are the experimental data. According to this theory, the adsorption behaviour can be explained by taking into account the vdW-interaction including the effect of thermal fluctuations.
1.5.2 Substrate Roughness

Adsorption on heterogeneous substrates has also been the subject of many researches [Che89, Kar90, Pfe89]. This implies that a certain roughness of the substrate results in bending the adsorbed film, this in turn increases the chemical potential of the adsorbate which leads to a larger thickness in comparison with the thickness on smooth substrates [And88, Rob91].

Figure 1.5: A typical isotherm obtained at \( T = 13.964 \) K for hydrogen on gold is plotted such that an FHH-isotherm (Eq. 1.3) would yield a straight line. The negative curvature is clearly visible. The solid curve is a fit based on the model from Mecke [Mec96]. The difference between the data and the dashed curve thus demonstrates the significant impact of thermal fluctuations on the liquid film thickness [Vor01].

Figure 1.6: Typical adsorption isotherms of argon on gold measured at the temperature of 84.22 K with quartz-crystal microbalance technique. The open triangles are the data points on a porous gold electrode. The squares are taken on a rough gold electrode. The inset shows the results of the corresponding FHH analysis. For illustration only part of the two adsorption isotherms are plotted [Bru80]. See Robbins et al. [Rob91] for a theoretical description of the isotherms on structured substrates.

1.6 Experimental Methods

Many different methods have been applied in the measurements of physisorption films. In all these methods, in general, the thickness of the adsorbed film as a function of vapour pressure (or chemical potential) is measured. The earliest and simplest method in this respect is the volumetric [Ma88,
In which the adsorption part is determined from the total amount of added gas. Also with the resonance microbalance technique, very precise measurements can be done. In this case the resonance frequency of a high quality mechanical oscillator is measured. Upon adsorption of an adsorbate on the oscillator the frequency changes proportional to the deposited mass. The oscillator is normally a quartz-oscillator with a thin film of the desired substrate evaporated on it [Kri84, Mig88, Mig86].

Specific heat measurements give extra information on the phase transitions in the physisorbed films [Zhu88]. For a direct measurement of the thickness, surface plasmon resonance [Eag79, Lei92, Her89] and ellipsometry [Nha87, Vol91, Hes91, Vol89] can be adapted.

The second group of measurements are often used to determine the structure of the adsorbed films. These measurements are often based on diffraction, such as neutron scattering [Lau91] and x-ray [Hai91] which strongly depend on the substrate under investigation. To have a measurable signal, substrates with relatively large specific surface (a few m²/g) are necessary. In addition, they should have a high coherence length. Coherence length here is equivalent to the dimensions of a crystallite on the surface. With small angle x-ray scattering the film growth can be monitored [Tid91]. Helium atom scattering is used on smooth substrates [Ker88]. With surface tunnel microscopy some investigations far below $T_\text{c}$ of the adsorbate have been done [Eig90].

In addition there are many material-dependent methods like nuclear-spin resonance [Pet89b], photoemission on metal surfaces [Far89], and measurements of third sound in superfluid helium [Zim92].
2 Wetting Phenomena

In this chapter the wetting phenomena of physisorbed systems are discussed. This begins by introducing the behaviour of a liquid drop on a solid substrate. Thereafter more advanced properties of wetting systems are introduced. Theoretical predictions are presented to understand the film behaviour near coexistence. Then experimentally observed transition phenomena are noted. It will be shown that in the majority of the physisorption systems, in which the vdW-interaction plays the dominating role, triple-point ($T_3$) wetting follows. In some exceptional cases other wetting transitions, which are discussed, can be observed. The important point related to this work is the behaviour of adsorbed films at equilibrium and near the $T_3$ of the adsorbate.

2.1 Thermodynamical Aspects

We consider the following system: a solid substrate, with a negligible vapour pressure, is fully or partly covered by a liquid (or solid) adsorbate. The substrate and the adsorbate can be of the same or different materials. The adsorbate coexists with its gas phase.

![Figure 2.1: The wetting behaviour of a drop is demonstrated near a solid surface. As explained in the text three different cases may happen under these conditions depending on the equilibrium values of the surface tensions. It should be noticed that in this case the effect of the substrate is neglected.](image)

If one brings a drop of an adsorbed material near a substrate surface, then different behaviours may be observed for the adsorbate-substrate system under thermal equilibrium. These behaviours can be specified with respect to a macroscopic contact-angle $\theta$. The contact-angle is defined as in Fig. 2.1. The contact-angle which is shown in this figure can best be defined via introducing the Young’s equation. The Young’s equation [You05] which describes the equilibrium of surface tensions in the system, is given by

$$\sigma_{lv} \cos \theta = \sigma_{sv} - \sigma_{sl}. \quad (2.1)$$

By definition $\sigma$ is the free energy cost per unit area (surface free energy) of forming a new interface. From Eq. 2.1 depending on the value of $\cos \theta$, three different scenarios are possensible:
1. $\cos \theta \leq -1$ : which means $\theta = 180^\circ$. In this case the drop beads up on the substrate and non-wetting (complete drying) follows. In the context of film growth this is called Volmer-Webber growth.

2. $-1 \leq \cos \theta \leq 1$ : which means $0^\circ \leq \theta \leq 180^\circ$. In this case incomplete-wetting occurs when the drop spreads somewhat on the surface. This is called Stranski-Krastanov growth.

3. $\cos \theta \geq 1$ : which means $\theta = 0^\circ$. The drop disappears by forming a thick flat film on the substrate, thus leads to complete-wetting or Frank-van der Merve growth.

Microscopically, even in the case of incomplete-wetting there always exist a thin film on the surface whose equilibrium thickness can be obtained from the effective surface potential. Some aspects of the wetting can be described together with the macroscopic contact-angle. For instance the type of a transition can be determined by applying conventional definitions and monitoring the behaviour of $\theta$ very close to a transition temperature $T_t$. In the following we introduce more theoretical advances.

### 2.2 Wetting Transitions

As noted before the wetting behaviour can be explained by surface tension $\sigma$. For adsorption on a surface, a thermodynamical differential equation for the surface tension can be written as

$$d\sigma = -SdT - \Gamma d\mu$$  \hspace{1cm} (2.2)

where $S$ is the surface entropy and $\Gamma$ is the excess surface density defined as,

$$\Gamma(T, \mu) = \lim_{V, A \to \infty} \frac{N_V - \rho_g V}{A}.$$  \hspace{1cm} (2.3)

Here $N_V$ is the total number of atoms, which is limited by the substrate with a surface area $A$, in volume $V$. $\mu$ and $\rho_g$ are the chemical potential and the density in the gas phase.

Eq. 2.2 implies that, in the simplest case, there are two contributions that have to be taken into account when discussing the types of wetting phenomena. Both the energy cost of creating a new interface and the entropy contribution of the film should be considered. The contribution of the entropy always favours the increase of the film thickness (wetting). This suggests that the wetting now depends on the energy cost of making a new interface. If forming the new interface by adsorption does not cost energy then complete wetting will occur. In other cases, the two contributions from the entropy and the surface energy compete. So the occurrence of the wetting depends on the value of the surface energy. Considering the fact that the surface energy is temperature dependent, at a certain temperature, a wetting-transition can occur from incomplete to complete wetting [Sha97, Tab93].

Theoretically, a wetting transition was primarily predicted in 1982 by Pandit, Schick and Wortonis [Pan82]. It will be shown that wetting transitions are indeed phase-transitions, which in their theoretical formulation, the excess surface density $\Gamma$ has the role of an order parameter [Die88,
2.2 Wetting Transitions

Figure 2.2: (a) Surface diagram showing a continuous wetting transition. Below $T_W$ the walls are not wet, whereas, above $T_W$ they are. Three experimental paths are shown. (b) Behaviour of the excess surface density as coexistence is approached along paths 1 and 2. Along path 2, complete wetting occurs at coexistence. (c) Behaviour of the excess surface density at coexistence as a function of temperature. Critical wetting occurs as $T_W$ is approached from below [Sch90].

Sch90, Sul86]. With respect to the behaviour of the $\Gamma$ two different kind of transitions can be defined. Wetting transitions are either of the first- or the second-order. The second-order is also called a continuous phase transition.

2.2.1 Second-Order Wetting Transition

For a continuous wetting transition $\Gamma$ changes continuously and approaches to a transition point which is on a coexistence line in the phase diagram. The possible paths in the phase diagram are shown in Fig. 2.2a. In the figure, $\mu_0$ is the chemical potential along the coexistence line.

Practically, in a system with a fixed volume, $\mu$ can be changed through a variation of pressure or temperature. Fig. 2.2b shows the process of $\Gamma$ at constant temperature (adsorption isotherm). Below the wetting temperature $T_W$, upon approaching the coexistence line $\Gamma$, the thickness of the film remains finite (path 1). This is called incomplete wetting. Above $T_W$, $\Gamma$ diverges near the coexistence which is a transition from a finite thickness below the coexistence to an infinite thickness at the coexistence. This is called a continuous wetting transition.

In Fig. 2.2c the behaviour of $\Gamma$ as a function of temperature is illustrated. In this case, along the coexistence line, a transition from incomplete to complete wetting occurs. This transition, which is
2 Wetting Phenomena

Figure 2.3: (a) Surface phase diagram showing a first-order wetting transition. Below $T_W$ the walls are not wet, above $T_W$ they are. Four experimental paths are shown. (b) Behaviour of the excess surface density as coexistence is approached along paths 1, 2, and 3. Complete wetting occurs as coexistence is approached along paths 2 and 3. In addition, there is a jump in the excess surface density on path 2 when it crosses the prewetting line. This jump gets smaller as the prewetting line is crossed further from coexistence and vanishes completely at the prewetting critical point marked by the dot. The jump gets larger as the prewetting line is crossed closer to coexistence. (c) Behaviour of the excess surface density at coexistence as a function of temperature. A first-order transition occurs at $T_W$ at which $\Gamma$ jumps continuously to infinity [Sch90].

a continuous transition, is sometimes referred to as critical wetting\(^1\).

2.2.2 First-Order Wetting Transition

Fig 2.3 shows a first-order phase transition. Such a transition is always associated with a so-called prewetting-line, which meets the coexistence tangentially at $T_W$ [Hau83] and ends at a critical end-point. In Fig. 2.3a possible thermodynamic paths are demonstrated. Fig. 2.3b shows the process of the adsorption isotherms, resulting from paths 1, 2 and 3. Path 1, at a temperature below $T_W$, ends at a finite thickness (incomplete-wetting) at coexistence. Path 3, at a temperature above end-point of the prewetting line, results in a continuously diverging thickness (complete-wetting).

Along path 2 the prewetting-line is crossed. By approaching the prewetting-line, the thickness jumps

\(^1\)This, in general, does not mean the bulk critical point $T_C$. At $T_C$, a continuous wetting transition can also occur [Cah77, Ebn87]. See Hess et al. [Hes97] for recent discussions on this subject.
to a higher value but remains finite, increasing the chemical potential further causes a continuous
diverging of the film at coexistence.

Such a first-order phase transition is always associated with a hysteresis of $\Gamma$ at the prewetting-line.
This can be seen by moving to and from the coexistence along path 2. Finally, Fig. 2.3c illustrates
the wetting behaviour along path 4 at coexistence. Below $T_W$, the film thickness remains finite, and
at $T_W$, discontinuously jumps to infinity.

2.3 Experimentally Observed Wetting Transitions

In this section the wetting transitions or the wetting behaviours, which have been observed exper-
imentally, will be introduced. It will be shown that in most of the cases the $T_3$ wetting occurs.
The first-order transition has been observed for quantum adsorbates, like helium and hydrogen, on
very weak-binding substrates. The second-order phase transition near the critical point is recently
observed for organic adsorbates.

2.3.1 Triple-Point Wetting

Experimental investigations of wetting show that in the majority of systems, along the sublimation
curve of the adsorbate, only incomplete, and from the bulk triple-point, $T_3$, onward, complete wet-
ting, follows [Die88]. This behaviour is called triple-point wetting. The $T_3$-wetting was primarily
predicted by Schick, Pandit and Fischer [Pan83] in 1983 and confirmed experimentally just one year
later by Krim et al. [Kri84] for a series of adsorbates on Au(111). Since then, the $T_3$-wetting has
been observed for quite a number of systems [Dri86, Mig86, Bru88, Lys86].

In Fig. 2.4a a typical phase diagram of an adsorbate, near its $T_3$ is demonstrated. Below $T_3$, the
solid phase of the adsorbate is stable which wets the substrate incompletely. Above $T_3$, the liquid
phase wets the substrate completely. The resulted isotherms, when moving along paths 1 and 2, are
shown in Fig. 2.4b. If one follows path 3 along the sublimation curve of the adsorbate, a continuous\(^2\)
change of the film behaviour from an incomplete, below $T_3$, to a complete wetting, above $T_3$, will
occur. This process is illustrated in Fig. 2.4c.

From a phenomenological point of view, the adsorbate-substrate structural mismatch seems to be
responsible for this behaviour [Hus84, Git84], that is, there will be an extra contribution from the
corresponding free energy of the mismatch to the right hand side of Eq. 2.1. This, in turn, shifts the
equilibrium condition into the incomplete wetting state. At $T_3$ such a contribution from the structural
mismatch disappears again. This aspect is of crucial importance to the work presented here and will
be thoroughly discussed in the next chapter.

\(^2\)This should not be confused with a real continuous transition. If the wetting transition were continuous then the
thickness of the solid film would grow continuously upon approaching $T_3$. In fact, in this case, the thickness of the
solid remains almost constant upon approaching $T_3$. But it is a liquid layer which grows above the solid since arriving
at the gas-liquid coexistence (see Fig. 2.6).
For many systems, the growing of the thickness along thermodynamic path 3 (Fig. 2.4), can be described by vdw-interaction through

\[ d \propto (T_3 - T)^{-1/3} \]  

which is predicted by Nightingale et al. [Nig84] on the basis of the fundamentals of thermodynamics. Since the \( T_3 \)-wetting plays a dominating role in the experiments which are presented in chapter 6, we briefly review its theoretical basis.

We consider the system in which the liquid phase (solid phase) of the adsorbate shows complete (incomplete) wetting on solid substrates. Such a behaviour has been experimentally confirmed for various systems [Bie85]. In such a system the wetting behaviour should change at the melting point of the adsorbate. Along the sublimation line the melting occurs at \( T_3 \), i.e., the wetting transition takes place at \( T_3 \). The chemical potential \( \mu_{f,l} \) of the liquid film which interacts with the substrate through vdw-forces is given as the sum of the chemical potential of the bulk liquid \( \mu_l \) and the contribution
2.3 Experimentally Observed Wetting Transitions

Figure 2.5: Schematic phase diagram of an adsorbate. The gas-liquid coexistence line is extrapolated into the solid phase with a hypothetical wetting transition at $T_W$. Along path (1) a macroscopically thick solid film is built up continuously (this isotherm is above the roughening transition), while along path (2) only a thin liquid film is formed on the substrate. Path (3) is known as the triple-point wetting. There is no qualitative difference in the wetting behaviour between (3) and (4), therefore triple-point wetting corresponds to complete wetting. [Die88].


from adsorbate-substrate interaction $\mu_{vdW}$

$$\mu_{f,l} = \mu_l + \mu_{vdW}(d)$$ (2.5)

Although, thermodynamically, below $T_3$ only the bulk solid phase can be stable, a thin liquid film of thickness $d_l$ can exist on the solid film if the interaction with the substrate lowers its chemical potential until the difference in the chemical potentials of the bulk liquid and solid phases is compensated:

$$\mu_{vdW}(d_{l,\text{max}}) = \mu_s - \mu_l$$ (2.6)

The thickness of the liquid film can be obtained by extrapolating the chemical potential of the bulk liquid around $T_3$ (see Fig. 2.5). This was done by Conradt [Con96]. For a nonretarded vdW-interaction, he obtained

$$d_{l,\text{max}} = \left( \frac{\alpha}{h_s - h_l} \right)^{1/3} \left( \frac{T - T_3}{T_3} \right)^{-1/3}$$ (2.7)

$^3$A similar relation is derived by Krim et al. [Kri84]. In which the first bracket in Eq. 2.7, except the exponent, is replaced with $\frac{a/k_B T_3^2}{(d \ln P_0/dT)_s - (d \ln P_0/dT)_l}$. See also Albrecht [Alb92] for details of the discussion.
where $h_s$ and $h_l$ are the melting enthalpy of the bulk solid and the liquid at $T_3$, respectively. The temperature exponent "1/3" is a direct consequence of the long-range behaviour of vdW-interaction (see Eq. 1.2).

Eq. 2.7 implies that the liquid thickness, in contrast to the solid, diverges in the vicinity of $T_3$, as shown in Fig. 2.6. Secondly, even below $T_3$ a liquid film can be stable and its thickness is determined by the deviation of the temperature from $T_3$. This has been confirmed in neutron scattering experiments of methane films on magnesium oxide [Gay90] and X-ray reflection from argon on magnesium oxide [Rie96, Rie97].

### 2.3.2 Surface Melting

A close relationship to the subject of wetting is the so-called surface melting. This implies that near the melting point the formation of a microscopic fluid or rather fluid-like film on the surface of the solid phase is possible (see [Vee91, Das89] for overview). This kind of surface melting can be described as an incomplete wetting of a solid through its liquid phase, which at the triple-point completely wets. In a phenomenological approach Pandit and Fisher [Pan83] have found a relationship between the $T_3$-wetting and the surface melting of an adsorbed solid film. Accordingly, the adsorbed film for $T < T_3$ is a combination of solid and liquid phases. Monte-Carlo simulations
of Wagner [Wag96] for solid para-hydrogen predict the existence of a liquid state for the upper layers even at 7.5 K below the bulk $T_3$. In fact, quasi elastic neutron scattering experiments of adsorbed oxygen [Chi88], deuterium [Zep90], and methane [Bie90] films showed a behaviour which is consistent with the explanation of surface melting of the film.

The question of which solids show surface melting or how the thickness of the molten film depends on temperature and whether the film has the properties of a fluid or an amorphous structure are the subjects of current experimental and theoretical studies (see, e.g., [Die88]).

It should be pointed out that, in spite of all described aspects which can be found in the literature, the difference between melting and $T_3$ temperature has been ambiguous.

### 2.3.3 Critical Wetting

Critical wetting is a continuous wetting transition at the bulk critical temperature. By varying the temperature along the coexistence of the liquid-gas, a continuous changing of the wetting behaviour from incomplete (drop in coexistence with a thin film) to complete (macroscopic film without drop) wetting can occur. For the first time this was observed experimentally for the system of pentane on water [Rag96]. For other systems like hexane on water [Sha97] this effect can be observed by manipulating the strength of the hexane-water interaction by adding salt into the water. Near the critical point the temperature dependency of the film is given by

\[ d \propto (T_C - T)^{-1} \tag{2.8} \]

where $T_C$ is the critical temperature. See [Die91, She95] for more theoretical aspects of critical wetting.

![Figure 2.7: Adsorption isotherm of hydrogen on rubidium taken below and above the wetting temperature $T_W = 17.89$ K. For temperatures above the wetting temperature, a finite jump corresponding to prewetting is observed (see Fig. 2.3b). The isotherms have been vertically shifted for clarity [Mis94].](image)
2 Wetting Phenomena

2.3.4 First-Order Wetting Transition

This transition was firstly predicted by Cheng et al. [Che91] for a system of helium on cesium. Thereafter it was observed experimentally by Nacher et al. [Nac91] that cesium, at temperatures below the lambda-transition, is either incompletely or not wetted at all by superfluid helium. Until then it was assumed that liquid helium wets any substrate [Goo75]. The first hint of the observation of a prewetting transition was in the experiments of third sound by Ketola et al. [Ket92a, Ket92b]. The prewetting-line corresponding to this transition was thereafter measured by Taborek et al. [Tab92, Tab93] with quartz-microbalance. The article by Cheng et al. [Che93a] gives an overview of the state of both theoretical and experimental research in this field.

Adsorption of hydrogen and deuterium on alkali metals has also been investigated [Mis94, Che93b]. In agreement with the theoretical prediction, a first-order wetting transition is observed for the case of molecular hydrogen on rubidium, Fig. 2.7, and the prewetting line is determined, Fig 2.8. In this case the wetting temperature is somewhere above the $T_3$ of hydrogen. In contrast, on sodium, no first-order wetting transition but only $T_3$-wetting is observed. Up to now, for hydrogen on any other substrate the $T_3$-wetting has been observed.

![Figure 2.8: The phase diagram of the prewetting transition (see Fig. 2.7). The $\Delta \mu(T)$ is the chemical potential difference of the transition (relative to the saturation) at temperature $T$. The solid line is a nonlinear least square fit $-\Delta \mu = a(T - T_W)^\beta$. This gives $T_W = 17.89 \pm 0.04$ K and $\beta = 1.47 \pm 0.08$ in good agreement with the value of $\frac{3}{2} T$ deduced from the thermodynamic arguments [Che93b].]

2.3.5 Roughening Transitions

The roughening transition (also "layering transition") occurs at a certain roughening temperature $T_R$, at which the free energy of making layers on the surface disappears. At $T_R$, the adsorbed film transforms from an atomically smooth to an atomically rough state. Macroscopically, this transition has been confirmed in disappearance of the crystalline facets [Wol85, Hey87, Elb91]. On substrates with a high surface homogeneity like graphite, longwise growth of steps and roughening transition at low temperatures can be seen for various adsorbate-substrate systems [You93]. In contrast, for substrates with an inhomogeneous surface, e.g., for H$_2$ on thermally evaporated metal films [Mig88,
2.3 Experimentally Observed Wetting Transitions

Mis94, continuous growth can be seen. This has already been observed for different adsorbates [Kri84, Mig86]. It infers that the surface of an adsorbed film itself can be rough in the case of complete-wetting.
3 Solid Adsorbates

Up to now we have mainly discussed the adsorption and wetting phenomena of liquid adsorbates on solid substrates. We saw that, above $T_3$, a thick liquid film exists, i.e., complete-wetting happens. Below $T_3$, the major part of the film is in a solid state, dewetting follows by leaving a film of only a few monolayers on the substrate. This phenomenon is called $T_3$-wetting and is a well known behaviour of many noble adsorbates on solid substrates.

In this chapter we consider the theoretical aspects of the wetting by a solid adsorbate. The thickness of the solid adsorbate at temperatures well below its $T_3$ will be concerned, and the possible reasons of the suppression of the wetting by the solid adsorbate is investigated. There are two aspects that play dominating roles in the wetting of a solid adsorbate. They are the strength of the adsorbate-substrate interaction and the roughness profile of the substrate. It should be noted that both of these are crucial in the wetting of solid adsorbates. Because, a solid film, in contrast to a liquid film, cannot tolerate the induced-strain from the substrate underneath. The structural mismatch, i.e., different lattice constants of the adsorbate and the substrate, seems to be responsible for introducing stress into the solid adsorbate. This effect can be amplified by the nonideality of the substrate surface, such as the roughness profile, which eventually leads to dewetting of the substrate by solid adsorbate.

3.1 Substrate Effect on Wetting

We consider an adsorbed film, which in general includes solid and liquid layers, on a solid substrate. Using statistical mechanics, for fixed temperature $T$ and pressure $P$, an excess grand canonical free energy $\Sigma(T, \mu, l_s, l_l)$ per unit area relative to a non-wetting situation can be found. In $\Sigma$, $l_s$ and $l_l$ are the thicknesses of the solid and liquid parts of the film, and $\mu$ is the chemical potential. By definition, $\Sigma(T, \mu, l_s, l_l) = \Delta \Omega(T, \mu, \rho)/A$ and the grand canonical potential difference is equal to:

$$\Delta \Omega = \Omega(T, \mu, \rho) - \Omega(T, \mu, \rho_{ref})$$

where $\Omega = F - \mu N$, equivalently $\Sigma = f - \mu n$ on a 2D surface\(^1\). The total excess free energy may then be split into three different terms:

$$\Sigma_{total} = \Sigma_{Thrm.} + \Sigma_{GS} + \Sigma_C$$

where $\Sigma_{Thrm.}$ is the thermodynamic contribution to the free energy of the solid film. The term $\Sigma_{GS}$ includes the effect of the lateral-strain induced in the solid film by the substrate underneath. The term $\Sigma_C$ accounts for an extra compression of the film caused by the substrate roughness.

\(^1\)See appendix B, where $\Omega$ and other quantities are introduced explicitly. The $F$ and the $N$ are the Helmholtz free energy and the total number of particles in the system, respectively.
3.1 Substrate Effect on Wetting

Figure 3.1: Illustrated is the comparison between the result of the former theory by GS and those from Esztermann et al. [Esz02], for different roughnesses. The thickness of the solid film raises as the roughness scale vanishes. $h$ and $L$ are typical scales of the substrate roughness as explained in Fig. 3.2.

Eq. 3.2 implies that when there is no compression in the film, the total free energy reduces to $\Sigma_{Thrnm}$. The thermodynamic part can be written as

$$\Sigma_{Thrnm}(l_s, l_l) = \sum_{l_s}^{h} \phi(l_s, l_l)$$  \hspace{1cm} (3.3)

where $\phi(l_s, l_l)$ is the vdW-interaction potential. In principal, Eq. 3.3 is valid for temperatures close to $T_3$ and for thicknesses $l_s$ and $l_l$ larger than microscopic distances. But when $l_l = 0$, a priori, the theory can also be applied to the temperatures below $T_3$, provided the pressure is close to the sublimation pressure.

At distances larger than a few monolayers, the asymptotic behaviour of $\phi(l_s)$ becomes important. It can be shown that for relatively large $l_s$ (see Eq. 1.2):

$$\phi(l_s) \simeq -\frac{C_3}{l_s^3}$$  \hspace{1cm} (3.4)

This suggests that $\Sigma_{Thrnm}$ is a decreasing function of $l_s$, and diverges as $l_s \rightarrow \infty$ which corresponds to a diverging film thickness or complete-wetting. But as already discussed, this does not happen for solid adsorbates.

In 1994 Gittes and Schick (GS) [Git84] considered the role of the substrate on wetting by introducing a new term $\Sigma_{GS}$ into the total excess free energy function. This is the excess free energy cost from
the strain induced in the film by the substrate, and for a large, yet finite solid thickness \( l_s \), is given by

\[
\Sigma_{GS}(l_s) = -\frac{BS^2}{l_s^2} - \frac{2BS^3}{l_s^3}
\]  

(3.5)

where \( B = \frac{3E}{2(1+\nu)} \), \( E \) is the Young’s modulus of the adsorbed solid, and \( \nu \) is its Poisson ratio. The term \( S \) is the total reduced stress which is given by \( S = 0.229(R - 1.88)\nu \) with the \( \nu \) denoting a molecular length scale. The substrate strength, \( R \), is the ratio of the integrated strength of the adsorbate-substrate and adsorbate-adsorbate potentials.

Now, the total free energy of GS-theory is the sum of the first and the second terms in Eqn. 3.2. It can be minimized with respect to \( l_s \) to get the equilibrium layer thickness. Having this done one arrives at

\[
l_s = \frac{C_3}{BS^2} - 4S
\]  

(3.6)

which is in general a nondiverging thickness but its value depends on \( R \). In Fig. 3.1 the equilibrium thickness of the adsorbate is plotted as a function of \( R \). The solid curves illustrate the results of this theory. Another aspect of this theory, as can be seen in Fig. 3.1, is the occurrence of reentrant incomplete-wetting upon increasing the substrate strength. This has an important implication in preplating systems in which the interaction of the substrate with the adsorbate can be affected by launching a layer (a few monolayers) of another adsorbate. With the application of this method there exists the possibility of transition from an incomplete- to a complete-wetting through a change in the substrate strength [Kli00, Con96, Fle00b].

However, the experimental results do not follow the prediction of this theory. For instance, for solid hydrogen film on gold substrates dewetting always occurs for \( T < T_3 \). That means the thickness of solid hydrogen film becomes of the order of a few atomic monolayers. Whereas, according to the GS-theory a considerable film thickness of 100 Å (essentially complete-wetting) can be achieved for hydrogen on gold where \( R = 4.5 \) [Esz02] (see Fig. 3.1).

One possible explanation for the discrepancy could be that the GS-theory neglects the substrate roughness which is a property of real surfaces. As a result this causes an extra bending of the adsorbed solid film. A weakly bent crystalline sheet of width \( l_s \) costs the following elastic free energy per unit area [Lan86]

\[
\Sigma_C(l_s) = \frac{E\bar{G}}{24(1-\nu^2)}l_s^3.
\]  

(3.7)
The term $\Sigma_C$ is due to the substrate roughness [Esz02]. In Eq. 3.7, $\overline{G}$ is a measure of the roughness amplitude which is proportional to $h^2/L^4$ (see [Esz04] for details of the calculation). For typical substrates, the surface modulation varies on a characteristic lateral length scale $L$ which is much larger than a vertical valley to peak height $h$, i.e., $L \gg h$ (see Fig. 3.2). In addition, it is assumed that $L \gg l_s$. The resulted thicknesses on a substrate with different roughness scales are plotted in Fig. 3.1 in comparison with the GS-results. It can be realized that a finite roughness of the substrate surface decreases the thickness of the solid adsorbate significantly and the film gets thinner as the substrate roughness scale increases.
4 Experimental Techniques

In this chapter the principals of surface plasmon spectroscopy and ellipsometry, which have been applied to the major part of the measurements, are introduced. These methods have been well established and widely used in different fields of experimental physics. To be specific, only those aspects which are relevant to this work are previewed.

4.1 Surface Plasmon Spectroscopy

4.1.1 Principals

Surface plasmon is defined as the quantum of the oscillations of an electron gas near the interface of a metal-dielectric, and can be excited by an electromagnetic wave (light). The nonradiating oscillation propagates along the interface of metal and dielectric medium. A dispersion relation for the expansion of the surface plasmon wave parallel to the interface has been derived by Raether \cite{Rae86} and given by

\[ k_{sp}^x = \frac{\omega}{c} \left( \frac{\epsilon_D \epsilon_M}{\epsilon_D + \epsilon_M} \right)^{1/2} \tag{4.1} \]

where \( \epsilon_D \) and \( \epsilon_M \)^1 are the dielectric constants of the dielectric medium and the metal. The dielectric constants are, in general, frequency dependent. In Drude model and near the plasmon resonance \( \omega_p \), the dielectric constant of the metal can be written as

\[ \epsilon_M(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{4.2} \]

Eq. 4.2 means that, in a metal, the expansion amplitude of surface plasmon waves fall off exponentially over a specific length of the order of a few micrometer. The vertical component, with respect to the surface, of the surface plasmon wave vector is purely imaginary in both media,

\[ k_{sp}^z = i \frac{\omega}{c} \left( \frac{\epsilon_D^2 \epsilon_M}{\epsilon_D + \epsilon_M} \right)^{1/2} \tag{4.3} \]

^1In fact, in the case of metal the dielectric constant is imaginary, i.e., \( \epsilon_M = \epsilon_1 - i \epsilon_2 \) and \( \epsilon_1 < 0 \). And for gold and silver, on which the surface plasmon can very well be realized, \( \epsilon_2 \ll \epsilon_1 \) \cite{Bas85}. The neglecting of \( \epsilon_2 \) thus has no impact on the qualitative behaviour of dispersion relation but it is considered in numerical analysis. Furthermore, it is obvious that \( -\epsilon_M > \epsilon_D \) and we deal with the dielectric media which are nonabsorbing (\( \epsilon_D \) is real and has no imaginary term).

\(^2\omega_p = ne^2/\epsilon_0 m_e \) where \( n \) is the free electron density, \( \epsilon_0 \) is the vacuum permittivity, \( e \) and \( m_e \) are the electron charge and mass, respectively.
4.1 Surface Plasmon Spectroscopy

Figure 4.1: Dispersion curves of the light and the surface plasmon. Optical coupling of the surface plasmon to the evanescent wave (ω_{Laser}) can be achieved by total reflection. The ϵ_G is the index of refraction of the dense medium (prism) which at its interface the light is totally reflected. At the incident angle θ_{res} the evanescent wave can be coupled efficiently to the surface plasmon.

which implies that the vertical component of the electric field falls off exponentially with the distance (evanescent wave) in the half-space of the dielectric medium,

\[ E_z^{sp} \propto \exp(-k_z^{sp}z). \] (4.4)

Here z is the direction perpendicular to the interface. This equation represents two important aspects; firstly, it gives a measure of the sensitivity of the surface plasmon, i.e., the maximum dielectric thickness which can be detected by this method. This is of the order of the wavelength of the applied light source. In practical cases it is of course a shorter length. Secondly, the electric field of the applied light should have a component vertical to the interface, which implies using a p-polarized light for the surface plasmon spectroscopy.

The plasmon frequency of metals are typically in the UV-region, i.e., surface plasmons can propagate with optical frequencies (curve OP in Fig. 4.1). But Fig. 4.1 suggests that, at the metal-dielectric interface, the surface plasmon wave vector is always bigger than the wave vector of the light in the dielectric medium (curve \( \omega = \frac{C}{\sqrt{\epsilon_D}}k_x \)). Which means the two dispersion curves of surface plasmon and the light intersect at \( k_x = 0 \). In other words, under these circumstances, a coupling between the surface plasmon and the light wave vector is not possible.

One way of enlarging the wave vector of the illuminating photons is using evanescent waves (see Eq. 4.4), which exist in optical thin films under total reflection. Their wave vector, parallel to the
4 Experimental Techniques

Figure 4.2: Otto(a) and Kretschmann(b) configuration for direct optical excitation of surface plasmons [Rae86]. The illuminating light is reflected totally into the bulk of the prism. Then the created evanescent light, which its electric field falls off exponentially with the distance, couples to the plasmon field through the air gap(a) or the metal film(b).

The excitation of the surface plasmon (resonance) can be associated with a minimum in the total reflected intensity at the resonance angle. See [Rae86] for a detailed electromagnetic description of the optical excitation of surface plasmons.

It is worth noting that there are some more complicated ways of exciting surface plasmons (see, e.g., [Sam91, BB91]). They have special applications but are not relevant to the work presented here.
4.1 Surface Plasmon Spectroscopy

Figure 4.3: Calculated shifting of the resonance minimum (solid line) and the width at half minimum $\Delta \theta_{1/2}$ (dashed line) for surface plasmon on gold upon adsorption of a thin hydrogen film with a thickness $d$. The incident angle changes linearly with the adsorbed thickness. The width of the resonance curve (see Fig. 5.2) increases upon increasing the thickness. [Alb92].

4.1.2 Thickness Measurement

Measurement of the thicknesses of the dielectrics can be understood by recalling the fact that $k_s^p$ in Eq. 4.1, is a function of the dielectric constant. Suppose a growth of a dielectric layer is initiated on a metal surface, e.g., adsorption of hydrogen on gold. Then the effective dielectric constant of the medium changes due to the increased polarizability of adsorbed atoms within the plasmon field. As more atoms are adsorbed the effective polarizability and subsequently the dielectric constant increases. As a result, the dispersion wave vector of surface plasmon, compared to the film-free surface, shifts to higher frequencies. This implies that, to have an effective coupling, the incident angle at which the resonance occurs must also be increased (see Eq. 4.5). For thicknesses much smaller than the cut-off length of surface plasmons a linear relationship can then be deduced between the shifting of the incident angle $\Delta \theta$ and the adsorbed thickness $d$:

$$\Delta \theta = a (\epsilon_D - 1) \ d \ (4.6)$$

The typical value of the proportionality constant $a$ is about 0.01 degs./Å for surface plasmon on gold and silver at frequencies in the visible range. By precisely measuring the change in the resonance angle (resolutions better than 1/1000 degs. was possible in our experiments), resolving a fraction of an atomic monolayer is possible. A more precise calculation of the resonance shift can be done based on the Fresnel equations in a four-layer system model.
Fig. 4.3 shows the exact calculated shift of the resonance minimum $\Delta \theta$ for a film of molecular hydrogen on gold as a function of film thickness. The width of the resonance curve, which is a measure of the surface quality of the film, is also illustrated. The width of the resonance curve increases through the growth of the film, as would be expected. This is practically measured and the results are represented in chapter 6. The reason for it is that the film surface becomes rough at higher thicknesses (see section 2.3.5). This in turn leads to the damping of the surface plasmon thorough converting to photons at scattering centers. As a result, this causes broadening of the resonance-width.

4.2 Ellipsometry

In contrast to the surface plasmon spectroscopy, as far as the type of the substrate and the film thickness are concerned, there is no limitation to the application of ellipsometry. Surface plasmon spectroscopy, as discussed, can essentially be used only on the surface of a few noble metals. In addition, because of the short cut-off length of the evanescent electric filed in the case of surface plasmon spectroscopy, measuring thicknesses higher than a few hundred angstrom is not possible. These problems do not exist in ellipsometry, but its high sensitivity to the polarization effects may sometimes be problematic.

Ellipsometry has a diverse area of applications. For example, it is widely used in the characterization of vacuum-deposited films [Raa86] or in the study of the adsorption on different substrates [Ita91, Chr85, Rot45, Asp79]. Also it has been used in the investigation of metal surfaces [Mer63] and in the measurements of oxygen adsorption on silicon surfaces [Arc62, Arc65]. The theoretical aspects and the analysis of the experimental results of ellipsometry measurements have been the subject of many works [Dit55, Sax65, Arc63, Rob60]. In addition there are good reviews, such as those of McCrackin [McC63, McC69], in which the principals of analysing the experimental data are fully explained. In reference [McC69], a computational program was introduced which is quite useful for analysing the data using complicated formulas of ellipsometry with many parameters. The book of Azzam and Bashara [Azz87] should also be added to this collection in which a comprehensive study of the principals and the most important aspects of ellipsometry are discussed.

In the following, we consider the usual case of a transparent nonabsorbing film on a surface of a substrate. The substrate itself can in general be absorbent, i.e., it can have a complex index of refraction. In Fig 4.4 the situation is schematically illustrated. The ambient medium and the film are nonabsorbing. The substrate is considered to have a well defined surface, so more complicated situations such as scattering etc. are not significant.

Once again we briefly introduce those aspects of the ellipsometry which are in the scope of this work. Two linear approximation relations from which the film thickness can directly be obtained from the ellipsometry scale readings will be introduced. These are specially useful for the purpose of the investigations of this work since the measured thicknesses, which are presented in chapter 6, are within the limits of the approximation.
4.2 Ellipsometry

4.2.1 Principals

Polarized light incident upon a surface in any state of polarization can be represented as the sum of two plane waves: one in the plane of incidence (the \( p \)-component), and another perpendicular to it (the \( s \)-component). In general, upon reflection from the surface, there are changes in the relative phases of the \( p \)- and the \( s \)-components and in the ratio of their amplitudes. The change in the difference between the phases of the parallel \( p \)- and the perpendicular \( s \)-components upon reflection is denoted by \( \Delta \), and the factor by which the ratio of the amplitude of the \( p \)- and the \( s \)-components changes is denoted by \( \psi \). Symbolically, if the phase angles are written as \( \delta \) and the amplitudes as \( A \), the \( \Delta \) and the \( \psi \) are

\[
\Delta = (\delta_p - \delta_s)_{\text{reflected}} - (\delta_p - \delta_s)_{\text{incident}} \quad (4.7)
\]

and

\[
\psi = \arctan \left( \frac{A_p}{A_s} \right)_{\text{reflected}} / \left( \frac{A_p}{A_s} \right)_{\text{incident}} \quad (4.8)
\]

The ellipsometer measures the \( \Delta \) and the \( \psi \). These quantities depend on the optical constants of the surface, the angle of incidence of the polarized light, the wavelength of the light, its initial state of polarization, and the thickness and the refractive index of the film which may be present on the reflecting surface.

4.2.2 Film-Free Surface

The effect of reflection from a film-free surface on \( \tilde{\Delta} \) and \( \tilde{\psi} \) (bars refer to the film-free surface) depends on the ambient-film interface. By definition, the \( \tilde{\Delta} \) and the \( \tilde{\psi} \) (experimentally measured quantities) define \( \rho \), the ratio of the Fresnel reflection coefficient for the \( p \)- and the \( s \)-component waves, i.e.

\[
\rho = \frac{r_p}{r_s} = \tan \tilde{\psi} \exp(i \tilde{\Delta}) \quad (4.9)
\]

The general formula for the Fresnel reflection coefficients \( r_p \) and \( r_s \), for a reflection from the surface of a medium \( b \) into medium \( a \) at the \( a − b \) interface, are (can be found in any standard book in optics, e.g., [Hec98])

\[
r_p = \frac{n_b \cos \varphi_a - n_a \cos \varphi_b}{n_a \cos \varphi_b + n_b \cos \varphi_a} \quad (4.10)
\]

\[
r_s = \frac{n_a \cos \varphi_a - n_b \cos \varphi_b}{n_a \cos \varphi_a + n_b \cos \varphi_b} \quad (4.11)
\]

\(^3\)Strictly speaking, \( r_p = |r_p|e^{i\delta_p} \) and \( r_p = |r_s|e^{i\delta_s} \) where \( |r_p| \) and \( |r_s| \) are the amplitudes of the Fresnel reflection coefficients, as defined in Eqs. 4.10 and 4.11. \( \delta_p \) and \( \delta_s \) are the relative phase changes with respect to the incident phases for \( p \)- and \( s \)-component waves, respectively.
where \( n_b \) and \( n_a \) are the indices of refraction of the media, \( \varphi_a \) is the angle of incidence and \( \varphi_b \) is the angle of refraction. It is worth noting, since angles of incidence and refraction are related by Snell’s law, given by

\[
\cos \varphi_b = \sqrt{1 - \left(\frac{n_a}{n_b} \sin \varphi_a\right)^2}
\]  

(4.12)

the Fresnel coefficients of Eqs. 4.10 and 4.11 can all be written as functions of the optical constants of the medium bounding the reflecting interfaces and the angle of incidence in the ambient medium.

For a bare surface, consider Fig. 4.4 in which, \( d \), the thickness of the film goes to zero, the value of the complex index of refraction of the surface can, after substitution Eqs. 4.10 and 4.11 in Eq. 4.9 using Eq. 4.12, be calculated from the equation [Dit55]

\[
\tilde{n}_2 = n_0 \tan \varphi_0 \left[ 1 - \frac{4 \rho \sin^2 \varphi_0}{(\rho + 1)^2} \right]^{1/2}.
\]  

(4.13)

Where \( \tilde{\Delta} \) and \( \tilde{\psi} \) can, after substituting \( \rho \) in this equation and separating the real and imaginary parts, then explicitly be related to the optical constants of the substrate [Bor59, Sax65]:

\[
n_2^2 - k_2^2 = n_0^2 \sin^2 \varphi_0 \left[ 1 + \frac{\tan^2 \varphi_0 (\cos^2 2\tilde{\psi} - \sin^2 \tilde{\Delta} \sin^2 2\tilde{\psi})}{(1 + \sin 2\tilde{\psi} \cos \tilde{\Delta})^2} \right]
\]  

(4.14)

and

\[
2n_2k_2 = \frac{n_0^2 \sin^2 \varphi_0 \tan^2 \varphi_0 (\sin 4\tilde{\psi} \sin \tilde{\Delta})}{(1 + \sin 2\tilde{\psi} \cos \tilde{\Delta})^2},
\]  

(4.15)

where \( \tilde{n}_2 = n_2 - ik_2 \). \( n_2 \) and \( k_2 \) are the real and imaginary parts of the index of refraction of the substrate. The values of \( \tilde{\Delta} \) and \( \tilde{\psi} \) depend on the type of the substrate. That means, in the \( \Delta-\psi \) graph, for a certain material, the point corresponding to \( \tilde{\Delta}-\tilde{\psi} \) is unique. This is a significant aspect of ellipsometry for determining even unknown materials by measuring \( \Delta \) and \( \psi \).

### 4.2.3 Film-Covered Surface

In the presence of a film on the surface, the situation becomes more complicated. In this case \( \Delta \) and \( \psi \) depends on the interference of the wavelets reflected from the ambient-film and the film-substrate interfaces (See Fig. 4.4). Under these circumstances the many-fold reflections inside the film should be taken into account which implies (compare with Eq. 4.9)

\[
\rho = \frac{R_p}{R_s} = \tan \psi \exp(i\tilde{\Delta}).
\]  

(4.16)

In this equation \( R_p \) and \( R_s \) are the reflectances of the two component waves. These are sums of the beam reflected from the ambient-film interface and the beams refracted into the ambient after an
4.2 Ellipsometry

Figure 4.4: Usual phenomenon of reflection a ray of light from a surface covered with a film. The ambient medium and the film are supposed to be nonabsorbing. The phases of beams change upon each reflection from an interface. The phase changes when the light passes the adsorbed film should also be taken into account. From the total phase change the thickness and some other optical constants of the film can be obtained.

An infinite number of reflections between the film-substrate and the ambient-film interfaces. In terms of the Fresnel reflection coefficients, $R_p$ and $R_s$ are written as [Hea55, Azz87]

$$R_p = \frac{r_{01p} + r_{12p}e^{-2i\varphi}}{1 + r_{01p}r_{12p}e^{-2i\varphi}}$$

$$R_s = \frac{r_{01s} + r_{12s}e^{-2i\varphi}}{1 + r_{01s}r_{12s}e^{-2i\varphi}}$$

where $r_{01p}$ and $r_{01s}$ are the Fresnel reflection coefficients of the two component waves, for reflection into the ambient from the surface of the film at the ambient-film interface. Similarly, $r_{12p}$ and $r_{12s}$ are corresponding coefficients for reflection into the film from the substrate at the film-substrate interface.

Thus the resulting fundamental equation of ellipsometry is

$$\tan \psi \exp(i\Delta) = \frac{r_{01p} + r_{12p}e^{-2i\varphi}}{1 + r_{01p}r_{12p}e^{-2i\varphi}} \times \frac{1 + r_{01s}r_{12s}e^{-2i\varphi}}{r_{01s} + r_{12s}e^{-2i\varphi}}.$$  (4.19)

In Eq. 4.19, the thickness of the film appears only in the quantity $\varphi$. This is the change in phase of the beam (with ambient wavelength $\lambda$) caused by traversing the film of thickness $d$ and index of refraction $n_1$,

$$\varphi = \frac{(360/\lambda)}{d} (n_1^2 - n_0 \sin^2 \varphi_0)^{1/2} \text{ degs.},$$  (4.20)

where $\varphi_0$ and $n_0$ are the angle of incidence in the ambient-film and the index of refraction of the ambient.

Substitution of Eq. 4.20, using the Fresnel reflection coefficients, into Eq. 4.19 and separation of the resulting equation into its real and imaginary parts yields one equation for $\Delta$ and one for $\psi$. Both
**Figure 4.5:** Illustrated is the calculated $\Delta$ and $\psi$ as a function of the index of refraction and thickness of transparent films on silicon. Each curve corresponds to a film of fixed index of refraction with thickness increasing in the direction of the arrow. The thickness scales are marked off in 20° increments in $\varphi$. Thickness is given by $15.17/\left(\frac{n^2 - 1}{n^2 - 0.8830}\right)^{1/2}$ Å [Arc62].

Equations are functions of the angle of incidence in the ambient-film, the wavelength of the light, the index of refraction of the substrate, and the thickness and index of refraction of the film. All of these quantities are independently determined or fixed constants except for the properties of the film which can be obtained from ellipsometer measurements by solving (in general using numerical computation) the resulted equations.

Fig. 4.5 shows a graphical representation of the dependence of $\Delta$ and $\psi$ on the properties of transparent (i.e., nonabsorbing) isotropic films on silicon [Arc62]. In the figure the parameters $\varphi_0 = 70^\circ$, $\lambda = 5461$ Å and the complex index of refraction of silicon $\tilde{n} = 4.05 - i0.028$ at this wavelength are used for the calculation.

Each curve in Fig. 4.5 is the locus of points of increasing thickness for a film of fixed index of refraction. The arrow on a curve shows the direction of increasing thickness and the underlined number is the index of refraction of the film. A thickness scale is marked off on each curve in 20° increments in $\varphi$. Eq. 4.20 may be used to convert these values from degree to angstrom units. The $\varphi$ scales for all of the curves have a common origin at $0^\circ$ which is the $\Delta$, $\psi$ point characteristic of a film-free silicon surface. The parameters $\Delta$ and $\psi$ are the cyclic functions of thickness and the curves repeat periodically with every $180^\circ$ change in $\varphi$. As an example for a film with an index of
refraction 1.5, the period is 2340 Å.

**4.2.4 Linear Approximation Method**

As discussed in previous section, there exist exact relationship between Δ and ψ and the properties of the surface film (Eq. 4.19). This equation in which the film is characterized by a thickness and an index of refraction, allows determining the dependence of Δ and ψ on the film properties. However, first-order approximate equations which are accurate for very thin films (thicknesses much less than wavelength of the light λ) can be derived and allow an easier illustration of the properties of the relationships [Arc65, Arc63].

In this work, for the computation of the thickness of, mainly, hydrogen films adsorbed on silicon which are presented in chapter 6, we adapted the two linear approximate equations from Archer [Arc65]. For the ratio of the Fresnel coefficients, first-order theory gives [Leb39, Bor33],

\[
\tan \psi \exp(i \Delta) = \tan \bar{\psi} \exp(i \bar{\Delta}) \left(1 - \frac{i 4\pi \cos \varphi \sin^2 \varphi}{\lambda \left(1 - \frac{1}{n_1^2}\right) \left(\cos \varphi - \frac{\sin^2 \varphi}{n_2^2}\right)} \left[\left(1 - \frac{1}{n_1^2}\right) - \frac{1}{n_2^2}\right] (n_1^2 - 1) d\right).
\]

This equation, after equating the real and imaginary parts on both sides, results in two linear equations

\[
\Delta = \bar{\Delta} - \eta d \tag{4.22}
\]

and

\[
\psi = \bar{\psi} + \gamma d, \tag{4.23}
\]

where the explicit forms of η and γ are given in appendix A.

For the experiments which are carried out in this work the thickness coefficients η and γ are constant and are calculated for fixed \( \varphi = 45^\circ \), \( \lambda = 6328 \, \text{Å} \), \( n_2 = 3.87-0.075 \) [Lid99] and \( n_1 = 1.13 \) (index of refraction of hydrogen film) to be \( \eta = 0.01856 \, \text{degs./Å} \) and \( \gamma = 1.216 \times 10^{-5} \, \text{degs./Å} \). In the experiment, the maximum precision with which Δ and ψ can be measured is about 0.005°. It follows that for film thicknesses measured here, the changes in ψ are not significant, but changes in Δ, as small as 0.268 angstroms in film thickness, can be measured. In reality, because of thermal fluctuations and birefringent effects, the precision is less than the predicted value.

In the end, it is worth noting that a reasonable criterion, for the validity of the linear approximation theory for very thin films and for the validity of the concept of index of refraction, is that the film thickness be large compared to the dimensions and separations of the constituent atoms or molecules. The above approximation is not valid for measuring monolayer growth since in this stage the index

---

4The first of such an approximation was made by Drude [Dru89, Hea55] which is adequate for thicknesses up to 10 Å. These have been corrected to be adequate for thicker films [Sax65].
of refraction is highly dependent on the thickness, i.e., it is not realistic to find an average index of refraction for the monolayer.
5 Experimental Setups

In this chapter we introduce the two experimental setups which we used in our measurements. The principals of the measurements were already discussed in the previous chapter. The surface plasmon spectroscopy setup with its optical components and signal processing facilities is described. A practical plasmon resonance curve is shown. Thereafter the null-ellipsometry setup together with the auxiliary components of laser annealing and laser heating is represented. The method of extracting the parameters Δ and ψ from ellipsometer rotational components, analyser and polariser, is explained. A short explanation of laser annealing is given by illustrating an annealing curve obtained on silicon. Finally, the construction of the cryostat and the measuring cell are described.

5.1 Surface Plasmon Spectroscopy

In Fig. 5.1, the surface plasmon spectroscopy setup is demonstrated. The excitation of surface plasmons occurs in the Kretschman-configuration, as explained in the previous chapter. A parallel monochromatic light beam falls on a mirror, after passing through a polariser P which ensures the p-polarization of the light and is reflected from the mirror M which is fixed on a piezo-electric bimorph. With the help of a function generator the piezo-bimorph is driven to oscillate with a frequency of about a few hundred Hz, near its resonance frequency. By this way, the reflection angle of the outgoing light from the bimorph is modulated (θ(ω) = θ₀ ± A sin ωt, A is the excitation amplitude and ω is the frequency). The lenses L1 and L2 are positioned such that only the image of the point on the bimorph, where the light is reflected, is built at the prism-gold interface. This fulfills the condition that the beam hits the surface always at the same position even when the angle of incidence changes. Lens L3 focuses the reflected light coming from the base of the prism on a photomultiplier, which measures the excitation of surface plasmons from the reflected intensity.

Modulation of the incidence angle of light allows us to track the resonance angle at which the surface plasmon is excited. This is done by using the lock-in technique. With this technique even a small shift of the resonance angle, through a change in the dielectric constant, due to adsorption of hydrogen on gold, can be measured. When the shifting of the resonance angle becomes larger (larger thicknesses), the incidence angle must be adjusted correspondingly. This is done by using a stepping-motor facility which is coupled to a piezo-mirror that serves as an angle-adjustment mechanism. The stepping-motor controller receives the lock-in signal as an input and regulates the incidence angle, by rotating the stepping-motor such that within its resolution precision the resonance (minimum reflectivity) is always sustained. The adjustment of the resonance angle is then measured through the reaction of the stepping-motor. The width of the resonance at half minimum is measured by using a second lock-in amplifier which is set at the reference frequency 2ω₀. This is particularly useful for measuring the quality of the plasmon-curve, hence the surface quality of the adsorbed film (see section 4.1.2).
The light source is a small laser diode which is powered below its laser threshold. This is done primarily to avoid interference effects in the beam path which can be clearly seen if the laser power increases, and secondly to decrease the heat transfer to the substrate since in the case of resonance the light photons effectively create phonons in the metal film. The laser power is of the order of a few nanowatts.

Fig. 5.2 shows a typical resonance curve which is taken on the surface of gold. Adsorption of hydrogen causes a resonance detuning. This means the resonance minimum shifts to the side to compensate the detuning. Measuring of the shift of the resonance angle allows us to determine the average thickness of the film adsorbed on the surface. Using this method thicknesses of less than a monolayer up to a few hundred nanometers can be resolved.

For surface plasmon experiments, gold (purity 99.999%), which is thermally evaporated on the base of an optically polished BK7-glass prism\(^1\)(\(A = B = C = 8.0 \pm 3\) arcmin, polished to \(\lambda/4\)), is used as the substrate. A freshly made prism is used, so the cleaning was not necessary. Then the gold film is evaporated on it in a high vacuum chamber with a final pressure better than \(10^{-6}\) mbar at room temperature. The typical evaporation rate was \(4\) Å/s. The film thickness is about 450 Å which is the optimal gold thickness for producing a highly sensitive plasmon resonance.

The average roughness (rms) of the gold substrate is about 1.3 nm [Hwa92]. More precise measurements show a strong preferred orientation of the crystallites with the (111) axis vertical to the

\(^1\)Melles-Geriot
5.2 Ellipsometry and Laser Annealing

Figure 5.2: An experimental surface plasmon resonance curve on gold. Reflectivity vs relative angle of incidence with respect to resonance angle is plotted. The resonance (minimum) shifts upon adsorption. The resolution at the resonance depends on the narrowing of the width at half minimum (width at half maximum if the absorption were plotted) of the resonance curve. The resonance angle is larger than the angle of total reflection as discussed in the previous chapter.

For measurements on silicon, a standard null-ellipsometry setup, which works based on the minimization of the reflected intensity upon reflection from the surface [Azz87], is built up.

In Fig. 5.3, the schematic drawing of the ellipsometry setup is shown. The ellipsometer is in the standard PCSA-configuration, where P, C, S, and A stand for polariser, compensator, sample, and analyser. In our setup, a quarter-wave (λ/4) plate is used as compensator and silicon serves as substrate. The main components of the ellipsometer have a stronger contrast. In a conventional null-ellipsometer, the minimum (null) intensity, detected by a photodetector PM, can be obtained by properly setting the analyser and polariser. Then, during adsorption the continuous rotational adjustment of the analyser and the polariser allows one to stay always at the minimum. The other optical components of the ellipsometer are in general fixed during one measurement but they may be adjusted for optimization purposes before taking measurements.

As noted in the previous chapter the practical point of ellipsometry lies on the determination of Δ and ψ from the polariser and the analyser scale readings. From those readings, the thickness of the
Figure 5.3: Setup of ellipsometry (solid path), laser heating (dotted path) and laser-annealing (dashed path). The main components of the ellipsometer are drawn with a stronger contrast. The system works in PCSA-configuration, where P, C, S, and A stand for polariser, compensator ($\lambda/4$), substrate (Si), and analyser. The first polarizer next to the laser source (1) is used both to ensure the polarization of the beam and to adjust the incident intensity on the substrate. The symbols PD, PM, and L stand for photo diode, photomultiplier, and lens. Laser heating (2) is used in order to locally perform the desorption-adsorption of the adsorbed film. With the help of laser annealing (3), which allows an effective surface cleaning of the substrate, we were able to melt the silicon.

film can be determined by using the formula given in the previous chapter. These are thoroughly discussed in the article by McCrackin et al. [McC63] from both the practical and the theoretical point of view. See also [Asp74, Sch70, Mat74] for discussions on optimizing the precision of ellipsometric measurements. For the configuration shown in Fig. 5.3, we obtain $\Delta = \pi/2 + 2P$ and $\psi = A$ with the compensator having a perfect relative retardation of $\pi/4$. The maximum thickness of the adsorbed film (hydrogen or deuterium in this work) is proved, through surface plasmon measurements, to be of the order of a few tens of angstroms even in the thick film regime. Thus this allows applying the linear approximation relations derived by Archer [Arc63] for calculating the coverage in the thin film regime (see section 4.2.4). We note that this approximation holds provided the film thickness does not exceed the 100 Å limit. At this thickness a maximum error of the order of one monolayer is expected [Sax65].

The null-ellipsometery setup works in the so-called self-compensating mode. That means the adjustment of analyser and polariser is such that the detected reflectivity on the photomultiplier (PM in Fig. 5.3) is always kept at minimum. This is done by fixing the analyser and the polariser in two mounts which can be rotated by rotary measuring stage (OWIS DT65). The motors are controlled through a PC and have an adjusted sensitivity less than 20 arcsec. The PC receives continuously the output of the photomultiplier through an AD-interface, then it rotates the analyser and the polariser till a minimum is achieved. Rotating the analyser and the polariser can be done spontaneously or
5.2 Ellipsometry and Laser Annealing

Figure 5.4: Silicon reflectivity on annealing. The reflectivity of solid silicon is about 30% and about 70% for molten silicon at visible frequencies. Upon illumination the temperature of the silicon rises within a few nanoseconds by absorbing the pulse energy. This results in melting of silicon which corresponds to an increase in reflectivity. The reflectivity remains at this value (plateau on the curve) a few hundred nanoseconds depending on the power of the pulse. The silicon then starts to recrystalize as the heat dissipates and the reflectivity gets back to the original value before annealing. The dotted curve is the ruby pulse which is slightly shifted in time for clarity.

The annealing equipments are used in order to study the effect of in situ cleaning and annealing of silicon on the wetting behaviour of adsorbates. In conventional low temperature physics, the substrate can adsorb water or other dirt during preparation, mounting and also cooling procedures since, e.g., the mounting of the substrate is done in the air. One way to get ride of these things is

one at a time depending on the application purposes. This setting is quite adequate for adsorption measurements but not for systems in which the changes are much faster than the response time of the setting. The lenses are used for better focusing of the beam on the substrate. Since they stand vertically in the path of the light, they do not affect its phase upon reflection from their surfaces [Azz87]. In addition to the ellipsometer, a 10 mW continuous wave (cw)-laser, $\lambda = 532$ nm (source (2) in Fig. 5.3) is used as a heating laser which allows the local desorption-adsorption of the film on the substrate at the spot where ellipsometric studies are done (see Fig. 5.3). The main reason for using this is to eliminate the birefringent effects (these cannot be avoided because, to do measurements on the substrate surface, the beam should pass through, at least, eight glass windows and each of them can change the state of the light upon putting small stress on it) which contribute to the phase changes. This causes shifting of the ellipsometry signal. The contribution of such artificial effects can be eliminated by desorption and adsorption of the film in a time that is shorter compared to the relaxations. Thereafter, by measuring this difference, the correct thickness of the film can be obtained.
heating of the substrate during and after cooling inside the cell. By using laser annealing method, heating can be done very effectively. Since in this case the annealing is localized, a much higher heating temperature, eventually melting of the substrate, can be reached.

Fig 5.4 shows the annealing results on the surface of silicon at room temperature. Upon hitting a strong laser pulse from a nanosecond ruby laser to the silicon, in a few nanoseconds, the reflectivity of the solid silicon rises and reaches the value of the molten silicon (plateau in the figure). Depending on the power of the pulse, the reflectivity remains in this value for a few hundred nanoseconds and falls down to the value before annealing as the heat transferred from the substrate pulse dissipates into the surrounding. The melting temperature of silicon is about 2000 °C [Jel86, Bon93]. Under these conditions and after the recrystallisation, the silicon wafer should have a very clean surface with a well defined roughness profile.

The annealing setup is shown in Fig. 5.3 together with the ellipsometry setup. The pulse of a ruby laser (source (3) in the figure) is guided to the silicon surface through reflection from prisms and dielectric-mirrors at the position where the ellipsometry measurements are done. The two ultra-fast photodiodes PD (Laser Components FND-100) are used for reflection measurements. The signals are recorded with a 300 MHz digital oscilloscope (HP 54510B).

Silicon was supplied in the form of wafers (supplier: Wacker Siltronic Burghausen) with an rms-roughness of 0.3 nm and an oxide layer of 20 nm on it.

5.3 Cryostat and Measuring Cell

The surface plasmon spectroscopy measurements and ellipsometry are done in two different optical cryostats, i.e., in two different measurement cells. The two cryostats work, in principal, in the same way with a few differences. In general, the cryostat and the measuring cell in which surface plasmon spectroscopy measurements on the surface of gold are done have a smaller size than those which are used for the ellipsometry on the surface of silicon. In addition, the cryostat, which is used in ellipsometry measurements, is capable of reaching temperatures lower than 2 K. Whereas, with the one used for surface plasmon spectroscopy, the lowest temperature in which the cryostat can be stabilized is about 6 K. The temperature stability of both cryostates are in the range of a few mK. The one, which is used for surface plasmon spectroscopy measurements, shows an even smaller value of the order of 1 mK.

A full explanation on the construction of the cooling facilities, cryostat and the measuring cell which is used for surface plasmon measurements can be found in the PhD thesis of Albrecht [Alb92] and Vorberg [Vor97]. In the following we briefly introduce the setup which is used for ellipsometry measurements.

A home-made cylindrical copper cell with a diameter of 3.5 cm and a height of 4.5 cm is made of two pieces which are the body and cap of the cell. The cap is tightened to the body with miniature screws which are used to compress an indium O-ring seal. The fill lines, two 1.2 mm diameter CuNi-capillaries, are attached to the cell cap by force-fitting them through the tinny holes and are then soldered. Electrical contact-pins mounted also on the cap are feed through for thermometry and other electrical connections. On the side of the main body, there are four-fold-symmetric holes made for mounting quartz-glass windows. These serve as transparent media for optical measurements on
5.3 Cryostat and Measuring Cell

Figure 5.5: Structure of the cryostat with measuring cell in it. Liquid helium is supplied from the top into the cryostat. At the bottom, it is evaporated around the cell by an evaporizer and heater. From the top, helium is pumped back to the recovery line. The iso-vacuum is already pumped to reach an end pressure smaller than $10^{-5}$ mbar. This helps isolating the cold part of the cryostat from surrounding. Other facilities are used also for shielding thermal radiations from the outside. The cell sits in the center of the cryostat which, in turn, allows uniform cooling of the cell. The copper which is used for making the cell helps relatively quick thermal equilibration in all parts of the cell, so thermal gradients are avoided. The transparent windows allow performing optical measurements.

the sample surface. The copper holder on which the silicon wafer is mounted, is attached to the cap from inside. The substrate is mounted upright on the holder. The cell was tested to be leak tight.

The main improvement on this cell in comparison with the one which was used in surface plasmon spectroscopy is the way of mounting the windows. Instead of attaching the windows to the cell by using conventional epoxy glues, the windows are mounted using indium O-rings. Two indium rings are placed between a 3 mm thick window and the cell on one side and a small flange on the other side. Miniature screws are used to compress the indium seal. In this way, the amount of strain created in the glass is small. This becomes critically important for ellipsometric investigations. The windows have a diameter of 15 mm.

Thereafter the whole assembly is fixed inside a Janis He-flow cryostat, Fig. 5.5. The temperature is measured with two Cernox thermometers. The thermometer inside the cell is a CX-1050-SD-1.4L type and works from below 2 K to room temperature. The one on the cryostat is a DT-470-Sd-12A type and has a temperature range from 2 K up to the room temperature. The temperatures can be read out with a Neocera temperature-controller, model LTC11. The pressure inside the cell is measured with two MKS Baratron pressure gages, type 120: precision pressure gage with a resolution of $10^{-6}$ mbar for measuring pressures below 10 mbar and type 627B: Absolute pressure gage, for pressures above 10 mbar up to atmospheric pressure. The display is a two channel readout device (type PR4000F). The pressure gages determine the pressure at the end of the two capillaries at room temperature. This aspect is discussed in different papers, e.g. by Liang [Lin53] or by Takaishi and Sensui [Tak63], in which the existence of a pressure gradient as a result of a temperature-gradient
along a capillary is calculated. The conclusion is that a pressure gradient along the capillary can be
created only if the mean free path of the gas in the capillary is comparable with the diameter of it.
This calculation is done for the dimension of our capillaries and the temperature ranges in which the
experiments are done and gives a negligible pressure gradient inside the capillaries.
6 Results and Discussion

In this chapter the important achievements of the research are represented. The thickness of the solid hydrogen film at temperatures well below its triple-point \( T_3 \) is investigated in light of the recent theoretical predictions (see chapter 3). The experiments, apart from the investigations performed outside the cryostat, can, in general, be divided in two categories.

The first part of the experiments were done on the surface of gold by using the surface plasmon spectroscopy method. Physisorption systems were studied and some results which were obtained by others were reproduced. Thereafter a comprehensive set of experiments was done for systems which mostly include hydrogen and deuterium molecules on the surface of gold substrate. Some investigations are also done for the case of methane and argon on gold which are also used as preplating materials. Furthermore gold substrates were cleaned by focusing a laser beam on the surface. However, the effect on the wetting behaviour of the solid hydrogen was not significant. The roughness of the gold substrate was also improved in order to see whether it has an influence on the wetting behaviour. Mixtures of hydrogen and deuterium, in which the behaviour of a mixture compared to the pure system can be investigated, are also interesting. Phase separation may take place in systems of mixtures.

The second part of the investigations were done on the surface of silicon. Silicon is chosen since it should have a much better surface profile than gold substrates. Moreover, it is a good candidate for the use of surface cleaning applications like laser annealing on its surface. Changing the substrate also needed building up a new setup on which, on the one hand, ellipsometry can be realized and on the other hand annealing of the substrate with the use of a pulsed-ruby laser can be done. On silicon, the investigations are mostly concerned about hydrogen adsorbate, though there is one measurement for deuterium. Eventually, in a series of experiments it is further tried to improve the roughness of the silicon surface and to investigate its effect on the thickness of the solid hydrogen at lower temperatures. These last experiments, in this sense, are concentrated on annealing and their results are presented.

6.1 Investigations on Gold Substrates

Usually the investigations are started by taking an adsorption isotherm at a temperature well above the triple-point temperature, \( T_3 \), of the adsorbate under investigation. This means sufficient amount of gas is condensed into the cell till the saturation at gas-liquid coexistence is reached, and bulk liquid is formed at the bottom of the sample cell. After the adsorption isotherm is completed the cell was slowly cooled down to temperatures well below \( T_3 \). It is then warmed up to temperatures above \( T_3 \). Under these conditions the situation is very close to the thermodynamic equilibrium condition, and the cooling and warming paths are always along the coexistence line.
6 Results and Discussion

Figure 6.1: Typical adsorption isotherm of hydrogen on gold taken at $T = 15$ K, well above the $T_3$ of hydrogen. The thickness $d$ (solid squares), plotted versus reduced pressure $P/P_0$, grows very fast just in the beginning because of the strong attraction of gold substrate. Thereafter it grows continuously and diverges, essentially complete-wetting, as the saturated vapour pressure, $P_0$, is approached.

6.1.1 Adsorption Isotherms Above $T_3$

The results discussed in this section are for the adsorption isotherms of hydrogen and deuterium on the surface of a 45 nm thick gold layer evaporated onto a glass substrate. The data were taken using the surface plasmon spectroscopy technique.

In Fig. 6.1 a typical adsorption isotherm of hydrogen on gold is shown. The film thickness $d$ versus the reduced pressure $P/P_0$ is plotted. The parameters $P$ and $P_0$ are the pressure and the saturated vapour pressure, respectively. The adsorption was taken by condensing sufficient amount of hydrogen gas into the cell till the saturated vapour pressure was obtained. This was done at $T = 15$ K which is well above the $T_3$ of hydrogen, 13.95 K. The saturated vapour pressure of hydrogen at this temperature is about 120 mbar. The thickness of the film increases as $P/P_0 \to 1$. In the adsorption isotherm curve, three different regions can be distinguished. In the beginning of the adsorption isotherm a step-like behaviour in the growth of the film can be seen. Thereafter the film grows continuously but with a smaller rate. In the pressure range very close to the saturated vapour pressure, the growing rate increases further and the film thickness at saturated vapour pressure diverges (complete-wetting).

For hydrogen molecules, which arrive at the bare gold substrate, the interaction between these molecules and the gold atoms is quite strong. This causes a relatively fast adsorption growth in
the early stages of the adsorption. An effect which appears as a step in the beginning of the adsorption isotherm. The thickness of the film at this stage is a few monolayers which has a nearly solid structure. Upon adding more hydrogen into the cell the film grows continuously. When the pressure inside the cell gets very close to the saturated vapour pressure the film grows steeply, so complete wetting of the surface occurs. Of course, under experimental conditions, because of gravitational and thermal fluctuation effects, the film thickness remains finite.

The thickness is measured, as explained in section 4.1.2, by shifting the surface plasmon resonance upon adsorbing of hydrogen. The width of the resonance increases as the film thickness increases on the surface of gold. This implies that the surface of the film becomes rough as the film grows (see appendix C, Fig. C.1). This is in agreement with theoretical predictions that capillary waves become significant as the liquid film thickness increases [Mec96, Vor01]. A similar behaviour is observed for adsorption isotherms of other adsorbates like deuterium, argon and methane which are investigated in this work. This suggests that above the triple-point of the respective adsorbate complete wetting occurs upon approaching the saturated vapour pressure. Also the surface of the film becomes rough as the film grows. For the case of argon and methane on gold the quick growth just at the beginning of the adsorption isotherm is not observed which means that the interaction of the substrate with these adsorbates is weaker than the case of hydrogen on gold. This is in agreement with theoretical predictions [Git84] and other experimental investigations [Fle00b].
In Fig. 6.2 the two adsorption isotherms of hydrogen and deuterium are compared. The growth of the film thickness is similar to the one shown in Fig. 6.1. The temperature at which the deuterium adsorption isotherm is done is 20 K, well above $T_3$ of deuterium which is about 18.85 K. The vapour pressure of deuterium at this temperature is about 290 mbar. There is no qualitative difference between these two isotherm behaviours. But in the intermediate region the thickness of deuterium is slightly thicker than the one of hydrogen. This may be understood together with the Frenkel-Halsey-Hill (FHH) phenomenological interpretation formula \[Frem49, Hal48, Hil49\], Eq. 1.3. In FHH, at a certain pressure ratio, the film thickness depends only on temperature and the Hamaker constant of the adsorbate. From this equation, the film thickness is obtained to be proportional to the cubic root of the ratio of the Hamaker constant $\alpha$ and the temperature $T$. The Hamaker constant of deuterium is shown to be higher than the one of hydrogen, whereas the isotherm of deuterium is taken at a temperature which is about 5 K above the temperature at which the isotherm of hydrogen is done. Both of these can affect the thickness of the film on the surface of gold at a certain pressure ratio. More investigations regarding this behaviour are required, and the role of thermal excitations may also be considered to draw final conclusions.

In Fig. 6.3 the adsorption isotherms of Fig. 6.2 are plotted in a logarithmic scale suggested by the FHH-model representation. According to the FHH-theory, a straight line should be obtained for an adsorption isotherm if the data points are plotted in logarithmic scale. It can be immediately realized that this does not necessarily follow its prediction.

In section 1.5 we discussed different reasons, such as substrate roughness and thermal fluctuations, for this deviation. Although, in the scope of this project, the effect of the substrate roughness on the adsorption isotherm behaviour is not investigated, we suspect that this can not be applied here since
6.1 Investigations on Gold Substrates

Figure 6.4: Temperature-dependence of the hydrogen film thickness adsorbed on gold. Above the triple-point, a thick liquid layer (complete-wetting) of hydrogen is formed on gold. Below it, the solid hydrogen dewets the gold substrate by leaving only a few monolayers. The cooling (solid circles) and warming (open squares) follow the same path. The data are obtained under equilibrium conditions as can be seen from the similar behaviour of the cooling and warming curves.

our gold substrates should be smooth enough for the case of adsorption isotherm. Moreover, most of those investigations are performed on the surface of fractally rough [Pfe89] or porous [Bru00] substrates which are different from our relatively well defined gold substrates.

As shown by Vorberg et al. [Vor01], deviations in the adsorption isotherm from the FHH predicted behaviour, which are observed in the intermediate region, can be explained by a contribution of thermally excited capillary waves [Mec96]. In our case, this seems to be more appropriate than the effect of substrate roughness since we have already shown how the resonance broadens as the liquid film grows near saturated vapour pressure.

6.1.2 Wetting Behavior Below $T_3$

As pointed out in the beginning of this chapter, it is of particular interest of this work to investigate the solid thickness in the temperature range below $T_3$. In our experiments this, soon after the adsorption isotherm was completed, is achieved by lowering the temperature well below the $T_3$ of the adsorbate. Under these conditions the film is in coexistence with the bulk material in the cell, and the cooling and heating are done along the sublimation line.
6 Results and Discussion

Figure 6.5: Shown is the data of Fig. 6.4 plotted in a logarithmic scale. Here $t$ is the reduced temperature, defined as $t = (T_3 - T) / T_3$, and $d$ is the thickness. As demonstrated a linear behaviour is obtained close to the $T_3$. From the two linear fits the critical exponents of the cooling and warming are $\beta = 0.27 \pm 0.008$ and $\beta = 0.26 \pm 0.005$, respectively. These values are in good agreement with the value of $1/3$ resulted from the theoretical calculation.

In Fig. 6.4 typical cooling/warming cycles for hydrogen on a gold substrate is shown. The rate of the temperature change is controlled to be about 20 mK/min, which ensures conditions close to thermodynamic equilibrium. The typical behaviour of dewetting is clearly observed at temperatures below the $T_3$ of hydrogen whereas above $T_3$ the adsorbed film is rather thick. The thickness drops steeply upon cooling below $T_3$ and eventually levels off at a value around 10 Å, corresponding to about 3 molecular monolayers, as the temperature is further lowered. The dewetting occurs during cooling of the cell (solid circles) at the point where the bulk solidification of hydrogen sets in. Since, at temperatures well below $T_3$, the major part of the film is solid, the dewetting of the substrate by the solid adsorbate can be concluded. This effect is reexamined by heating the cell to temperatures well above $T_3$ of hydrogen, and its results are shown (open squares) in Fig. 6.4. Upon approaching $T_3$, the hydrogen film thickness diverges which indicates complete wetting of the substrate. Since this is the liquid thickness which increases steeply near $T_3$ (see, e.g., Fig. 2.6), the complete wetting by the liquid phase occurs. The reversibility of the cooling and heating processes is a sign of the well established equilibrium conditions under which the adsorbed film is prepared. Some slight discrepancies in the film thickness during cooling and heating are considered to result from small thermal fluctuations during ramping down and up of temperature. It is notable that below $T_3$ the surface tension of the solid film is large and the film is stable to thermal excitations whereas when $T_3$ is approached the liquid, which has a rough surface due to the capillary waves, grows on top of it. This can be clearly observed in the broadening of the resonance width (see appendix C, Fig. C.2).
6.1 Investigations on Gold Substrates

Fig. 6.5 illustrates the same data in Fig. 6.4 in a logarithmic scale. This is primarily done in order to see to which extent the film behaves as a liquid and eventually to extract the critical exponent of the behaviour.

Let us shortly review the subject of the film behaviour upon approaching \( T_3 \) (see the discussion in section 2.3.1 for complete explanation). It is proved both experimentally and theoretically that for an adsorbed film at saturation only a few monolayers of the film in the vicinity of the substrate are solid (which determines the thickness at \( T \ll T_3 \)). Therefore growing of the thickness close to the triple-point is ascribed to thickening of the liquid layer on top of the solid. On this basis, one would expect that the temperature dependence of the liquid film thickness close to \( T_3 \), can be written as \( d(T) \propto [(T_3 - T)/T_3]^{-\beta} \), with \( \beta = 1/3 \) [Alb96]. This means that a liquid film will follow a "power law" near \( T_3 \) (plotting the data in double logarithmic scale results a straight line). In other words, whenever the solid thickness becomes significant, some deviations from this behaviour must be observed.

Fig. 6.5 suggests that the data of hydrogen are in agreement with the prediction of this theory. In the figure two linear fits are plotted for cooling and warming curves in the region where the linear behaviour is followed. The fits give the exponents \( \beta = 0.262 \pm 0.01 \) and \( \beta = 0.27 \pm 0.01 \) for cooling and warming, respectively. These values are in good agreement with the predicted value "1/3". The small deviation from the theoretical value could be due to nondiverging thickness of the film at \( T_3 \). This confirms, once again, that the solid hydrogen film on gold substrate is relatively thin as no deviation is observed from the linear behaviour at lower temperatures. For comparison, in Fig. 6.6, the wetting of deuterium on gold for both cooling (solid circles) and warming (open squares) is illustrated. A similar behaviour, like in the case of hydrogen on gold, can be seen. This means, forming a relatively thick film at temperatures well above \( T_3 \) of deuterium, whereas dewetting of the substrate occurs below \( T_3 \) by leaving only a few solid monolayers on the surface of gold. The cooling and warming curves follow the same path with negligible discrepancies. No matter how often the cooling or the warming are repeated, the overall wetting behaviour remains unchanged. The thickness of the solid deuterium, at temperatures well below its \( T_3 \), is slightly less than 10 Å, corresponding to roughly three monolayers.

In Fig. 6.7, the results of cooling and warming of deuterium are plotted in a logarithmic scale. It shows a good agreement with the theoretically predicted linear behaviour. From the linear fits, the critical exponents for cooling and warming are obtained as \( \beta = 0.30 \pm 0.005 \) and \( \beta = 0.29 \pm 0.005 \), respectively. These are even in better agreement with the theoretical value "1/3" than those of hydrogen.

At this point, a comparison between the measured solid thickness at \( T \ll T_3 \) and the prediction of theory appears adequate: for hydrogen on gold, the value of the reduced substrate strength is \( R = 4.5 \) [Esz02]. As seen from Fig. 3.1, for this value of \( R \), the solid film should be thicker than 100 Å, corresponding to 30 monolayers if we assume a smooth substrate as in the GS-theory [Git84]. From the fact that only a solid layer of about 3 monolayers is measured, we conclude that the substrate roughness plays an essential role here [Esz02] (cf. the dotted curve in Fig. 3.1).

This triple-point wetting behaviour has been observed to be universal for almost all van der Waals adsorbates, in particular the noble gases [Mig86, Rie97, Mis99]. For instance, in our experiments we have investigated the situation for argon and methane and the same overall behaviour is observed. In the following we investigate some mixtures of hydrogen and deuterium.
6 Results and Discussion

Figure 6.6: Wetting of deuterium on gold is demonstrated. Like in the case of hydrogen on gold a thick liquid deuterium film can be formed on gold at temperatures well above the triple-point of deuterium. Whereas at temperatures below it dewetting takes place in the solid phase. This effect is reproducible as can be seen from cooling (solid circles) and warming (open squares) curves. Deuterium film in thick film regime, has a rough surface whereas in thin film regime, it is smooth.

6.1.3 Mixtures of Hydrogen and Deuterium

The idea of using mixed systems of hydrogen and deuterium occurred to us after doing preplating of hydrogen by deuterium. As explained before, preplating means depositing a few monolayers of another adsorbate on the surface before doing the adsorption of the main adsorbate under investigation. By doing so, the interaction between the substrate and the adsorbate can be tailored, and by choosing a proper preplating material an effective substrate strength $R_{eff}$, which is smaller than the $R$ without preplating, may be achieved. As a result this could lead to complete wetting of the substrate by the solid film (see Fig. 3.1). This is another aspect of the GS-theory, which predicts a different solid thickness depending on the type of preplating adsorbate [Git84].

For hydrogen on gold, preplating with argon, neon and methane have already been done some time ago [Kli00]. Similar experiments followed for deuterium on aluminium and graphite (HOPG) with argon, neon, methane and C$_2$H$_6$ [Fle00b]. Although, in some cases, a slight increase of the solid thickness was achieved, the overall effect of dewetting by the solid film continued to exist [Kli00]. We have also studied the effect of argon and methane preplated gold on the wetting behaviour of hydrogen. Our results agree with previous experiments.

Preplating with deuterium is done by taking adsorption isotherms of deuterium at 20 K, above its $T_3$ (cf. $T_3$ for pure deuterium is 18.85 K). Having established saturated vapour pressure, the sample is
6.1 Investigations on Gold Substrates

Figure 6.7: A logarithmic plotting of the data in Fig. 6.6 is illustrated. Here, $t$ is the reduced temperature and $d$ is the thickness. A linear behaviour is obtained in good agreement with the theoretical prediction for a layer of liquid close to the triple-point of deuterium. Solid and dotted lines are fits to cooling and warming data, respectively. The fits give the values $\beta = 0.29 \pm 0.003$ and $\beta = 0.30 \pm 0.003$ for the critical exponents of the cooling and warming curves, respectively. The theoretical prediction for the critical exponent is equal to "$1/3$".

cooled down to 10 K, Fig. 6.8. At $T \ll T_3$, the preplated thickness of deuterium is about 3 monolayers, quite similar to hydrogen. After warming up to 15 K, an adsorption isotherm of hydrogen until reaching saturated vapour pressure, is taken. At saturation there are a few tens of monolayers of liquid hydrogen on top of the preplated solid layers of deuterium on gold. Then the cell is cooled down to 7 K and the typical dewetting behaviour is observed, see Fig. 6.8. However, this time there is no distinct change at the expected triple-point of pure hydrogen but only the usual decrease in film thickness. Warming up to 15 K shows a small change in the dependence of the hydrogen thickness on temperature, hereby a hysteresis develops for $T > 13$ K, which increases as the temperature rises. This indicates that there is already some partial mixing between the hydrogen and deuterium molecules which, as a result, shifts a possible existing dewetting-point to higher temperatures.

In order to establish a complete mixing of hydrogen and deuterium the temperature is then increased and stabilized at about 30 K. A hydrogen-deuterium mixture with certain species concentration is so prepared at this temperature. Having both components in their gas phases ensure a good homogeneous mixture. After leaving the system at this temperature for several hours the cell is slowly cooled down to study the dewetting and to map out a possible effective triple-point of the mixture. The speed at which the temperature is changed is, as before, about 20 mK/min. The results of these experiments are presented in Fig. 6.9 in which the dependence of the film thickness on temperature
for two different concentrations of deuterium in hydrogen, as well as for the pure deuterium and pure hydrogen case are shown. To establish this variation in concentration we just add more hydrogen after reaching the saturated vapour pressure of hydrogen during the adsorption isotherm, and the above procedure is repeated. As can be seen in Fig. 6.9, there is a dewetting behaviour similar to pure hydrogen or deuterium, but with a shifted effective triple-point, $T_3^{(eff)}$, which falls always between the $T_3$’s of pure hydrogen and pure deuterium depending on the species concentrations.

In Fig. 6.10 the results of a series of experiments are illustrated. However, using these mixtures does not alter the dewetting behaviour below $T_3$. In addition, no significant change in the thickness of the solid layer is observed. But, in the region very close to the triple-point there is a pronounced hysteresis between cooling and warming. This behaviour is not observed for pure isotopes. A comprehensive analysis of this phenomenon together with some investigations of systems composed of other mixing ratios of hydrogen-deuterium are presented in the paper by Tibus et al. [Tib03].

As a consequence of these preplating and mixture experiments we conclude that the dewetting below $T_3$ is a rather robust phenomenon which, for the substrates discussed so far, hardly depends on properties like the details of the interaction strength. This suggests that a more general aspect should be dominating here. It will be shown in section 6.2 that the key to the problem appears to be the substrate roughness, as already indicated theoretically.
6.1 Investigations on Gold Substrates

Figure 6.9: Adsorbed film thickness as function of temperature (for clarity only the warming-up curves are shown). From left to right: pure hydrogen, 50% (deuterium)–50% (hydrogen) mixture, 75% (deuterium)–25% (hydrogen) mixture, and pure deuterium. In the legend $n_D/n_H$ indicates the molar ratio of deuterium and hydrogen in the mixed system. The drastic increases of the film thickness pinpoint the effective triple point, which is $16.4 \pm 0.01$ K for $n_D/n_H = 1.0$ and $17.5 \pm 0.01$ K for $n_D/n_H = 3.06$ mixed systems. Uncertainty in the absolute thickness is less than one monolayer.

6.1.4 Effect of the Substrate Roughness on Wetting

Before manipulating the surface roughness of the substrate, it was cleaned. Contamination, here, means, e.g., water on the surface which condenses either during preparation and mounting of the sample or during cool down of the system. Other types of contamination may exist, but are less likely since the sample cell is always kept under high vacuum. Thereby, we laser-heated the surface under study during cooling from room temperature till reaching about 50 K. This was done with a beam of a 220 mW green-laser directed onto the substrate, exactly at the point where surface plasmon spectroscopy investigations were done. No difference in the wetting behaviour was observed, neither for the adsorption isotherms nor for the temperature scans between the heated and nonheated gold surfaces. Although the efficiency or the completeness of the cleaning process may still be discussed, at least, we got rid of the most probable contaminate water.

Hence, the important factor, causing triple-point dewetting, might be the roughness of gold substrate. With this in mind we produced smoother gold substrates. Instead of preparing the gold substrate in the standard way of direct evaporation on the base of the glass prism, (see Fig. 6.11a), another method is used. A commercial silicon wafer, which serves as a quite flat template, was chosen. Thereafter a gold film of the same thickness as previous samples was evaporated on its surface. The glass prism, used as a support for the gold film in the surface plasmon resonance measurement,
Figure 6.10: Dependence of the effective $T_3$ on the concentration of deuterium. It can be seen that the effective triple-point of a mixture depends on the species concentration. For mixed systems, a hysteresis between cooling and warming curves is observed. This suggests that, in contrast to pure systems, the effective triple-points during cooling and warming may be different. From this, a phase diagram for the mixed systems may be extracted.

was then glued onto this film, and after removing the silicon wafer, the surface of the gold film had essentially the roughness of the wafer, as shown in Fig. 6.11b.

The surface profiles of the substrates, demonstrated in Fig. 6.11, were analysed by atomic force microscopy (AFM). As can be seen, the gold substrate, which is originally prepared on the surface of silicon wafer has a smoother surface profile. But, in spite of the reduced roughness of such a surface, the wetting behaviour of hydrogen on both of them remains approximately similar.

To find out why the wetting behaviour shows no difference, in spite of all efforts to prepare a smoother substrate, the AFM results were further analysed theoretically. The related theoretical parameter concerning the roughness of the surface is the so-called geometrical factor $\overline{G}$, introduced in chapter 3. If the roughness is really improved, then two different $\overline{G}$’s should be obtained for the substrates. The calculated values are $\overline{G} = 5.4 \times 10^{-4}/\varsigma^2$ and $\overline{G} = 2.2 \times 10^{-4}/\varsigma^2$ for the AFM pictures of Fig. 6.11a and Fig. 6.11b, respectively.

The theoretical analysis reveals that, although the roughness of the substrate seems to be optically improved, the roughness on the microscopic scale appears to be unchanged. The values of the $\overline{G}$-factor suggest that the roughness of both substrates are essentially of the same order of magnitude, but the one, which is prepared on the silicon wafer, has a slightly smaller roughness amplitude. This eventually leads to a difference of about 15% in the thickness of the solid film, which may be confirmed experimentally if the thickness is measured with a very high resolution.
6.2 Wetting Investigations on Silicon

The choice of silicon as a possible substrate for investigations of physisorption systems was based on the aspects which are critical in the non-wetting regimes. The most important reason for this is the better roughness profile of a silicon substrate compared to the gold substrates prepared on glass. The AFM analysis of both substrates shows that a normal gold substrate has a typical rms roughness of about 1.3 nm whereas, for commercial silicon wafer surfaces, this is ∼ 0.15 nm [Ang03]. Another reason is the strength of van der Waals interaction of hydrogen on gold and silicon substrates. The van der Waals interaction has already been calculated for hydrogen and other noble adsorbates on silicon surfaces [Mul87]. Yet, a gold film dewets the glass. In some previous experiments by others, the gold substrate was preplated with a thin layer of chrome. The aim of the preplating was to increase the wettability of the gold film which may result in a better roughness of the gold surface. Even this has not had any effect on wetting behaviour of hydrogen.

Figure 6.11: a) Atomic force microscope (AFM) image of a gold film evaporated on a glass prism at room temperature; the upper graph shows a line scan of the image. b) With the same resolution generated AFM-image of gold, however this time initially evaporated onto a silicon wafer, thereafter is detached from the silicon onto the glass prism (see the text for details). A typical line scan is shown again in the upper part. As can be seen, compared with the image on the left, the roughness of the gold has clearly improved on micrometer scale. But, the characteristics of the roughness on microscopic scale seem to be unchanged.

Thus evaporated gold films, although optically smooth, appear rough on the atomic scale which is relevant for the wetting behaviour (see section 6.1.4). As a result, we are interested in substrates which have an even smoother roughness profile. In this respect, silicon seems to be a good candidate.

6.2 Wetting Investigations on Silicon

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1Preparation of gold surfaces using thermal evaporation method on solid substrates, produces, in general, a quench-condensed gold film which is usually rough [Mul87]. Yet, a gold film dewets the glass. In some previous experiments by others, the gold substrate was preplated with a thin layer of chrome. The aim of the preplating was to increase the wettability of the gold film which may result in a better roughness of the gold surface. Even this has not had any effect on wetting behaviour of hydrogen.
6 Results and Discussion

Figure 6.12: Adsorption and a few temperature scans of the hydrogen on silicon. $\Delta$ is measured with respect to the value of the film-free silicon surface. The horizontal dotted line is an imaginary line which illustrates the surface of the silicon. At point A an adsorption isotherm is taken till saturated vapour pressure is reached at point B. Thereafter temperature sweeps were done. At lower temperatures shifting of the signal below the level of the silicon surface (point A) is clear. This can only be explained by taking into account the role of some artifacts which are discussed in the text. The noise in this figure is mainly due to mechanical vibrations, which were also present for the data in Figs. 6.13 and 6.14, but have been eliminated in the later runs.

different substrates [Vid81, Vid91, Rau82]. The interaction is nearly the same for hydrogen on gold and silicon. Using the calculations of Vidali and Cole [Vid81], we get 8739 KÅ$^3$ and 6276 KÅ$^3$ for the van der Waals interactions of hydrogen on gold and on silicon, respectively. Although these calculations assume perfect surface profiles for both gold and silicon substrates, estimated uncertainties of about 20%, arising from the applied approximations, should also be taken into account. The film thickness is proportional to the cubic root of the vdW-coefficient (see Eq. 1.2 or 1.3), so as far as the substrate strength is concerned, the wetting behaviour of hydrogen should essentially be similar on silicon and gold. It is therefore likely that, should differences in the wetting behaviour of our gold and silicon surfaces be observed, they can be ascribed to different surface topographies.

The third reason for choosing silicon as substrate is that silicon, in contrast to gold, can be cleaned by using laser annealing facilities.

6.2.1 Standard Method

Measurements on silicon are done by using ellipsometry as described in chapter 5. The configuration of our ellipsometer has been changed a few times in order to find the adequate setting for the experiment. The first ellipsometer used was a reflectometer which measured changes in the reflected
6.2 Wetting Investigations on Silicon

Figure 6.13: Corresponding development of $\psi$ in Fig. 6.12 with respect to the value of a bare substrate. Like in the previous figure, $A$ is the point where an adsorption isotherm is initiated. There is hardly any change in $\psi$, which is consistent with what one would expect. Upon ramping the temperature a small shifting is seen but its magnitude is much smaller than those in $\Delta$.

intensity upon adsorption and also temperature scans. By plotting these changes in intensity, one is able to estimate the relative state of the adsorbed film. But, making a statement on the real film thickness from these data was not possible. Therefore, it was necessary to adapt the null ellipsometry. This configuration is schematically shown in Fig. 5.3 and the results, which are presented here, were obtained with this setting.

Here, we will discuss the typical problems in using ellipsometry inside a cryostat specially at low temperatures. One of the critical problems which we were faced is drifting of ellipsometry quantities, i.e., $\Delta$ and $\psi$ during the sweep of temperature. This is, in fact, an artificial effect which, as noted before, occurred because of the high sensitivity of the ellipsometer to polarization effects, such as strain-induced birefringence in the quartz windows. As a result, the position of the minimum shifts, e.g., upon temperature ramping. The optical windows are normally mounted between metal pieces, so thermal contraction or expansion of these pieces upon cooling or warming can induce small strains in the glass window. This, in turn, caused a phase change in ellipsometry beam which passed through the windows. In Fig. 6.12 the progress of $\Delta$ in the course of a measurement upon a few temperature ramping is demonstrated. In the figure, $A$ illustrates the point where an isotherm of hydrogen on silicon is initiated at 14.7 K, well above $T_3$ of hydrogen. The horizontal dotted line thus corresponds to the surface of a bare silicon substrate before adsorption $\delta \Delta = 0$. Upon adsorption at this temperature the signal increases and reaches a value of about 1.50 degrees at saturation, point $B$.

\[^2\text{In our experiments $\Delta$ is always measured with respect to the value of it on bare silicon surface. By recalling the notation of the symbols in section 4.2.4 this can be written as $\delta \Delta = \Delta - \bar{\Delta}$. A similar relation valid for $\psi$ can also be written as $\delta \psi = \psi - \bar{\psi}$.}\]
In Fig. 6.12, we showed how effective ellipsometry is in showing wetting, but the artificial effects prevent us from making a reasonable judgment on the real film thickness. Here, we see that how significantly the temperature affects the signal.

Thereafter the temperature is adiabatically lowered near 11 K. At this temperature the quantity $\delta \Delta$ is obviously well below the level of the substrate surface. This is a clear sign of some artifacts which have contributed into the shifting of ellipsometry signal since, physically, it can not be interpreted. A closer look into the signal behaviour reveals that drifting of the signal starts from the beginning, as soon as the temperature scans start. In order to see whether the drifting of the signal stops at some point, the temperature was slowly ramped up and down three times (two times cooling and once warming) as shown on the figure. From the figure, it can be realized that the wetting curves follow different paths which means, on one hand, that the progress of shifting continues as the time passes, and on the other hand, the rate of the shifting is not constant.

In Fig. 6.13, the corresponding changes of the $\psi$, relative to the value of the film free silicon substrate, due to the birefringent effects are depicted. As in Fig. 6.12, the horizontal dotted line in Fig. 6.13 represents the level of the silicon surface. Again in this figure point A is the position where the adsorption isotherm is taken. As can be seen in the figure, the changes in $\psi$ are not significant as previously predicted (see section 4.2.4). Upon ramping the temperature, a drift in $\psi$ is seen although it is orders of magnitude smaller compared to the values of $\Delta$. A small modulation of the signal during the course of these experiments is because of some temperature instabilities which occasionally occurred in the laboratory.

To be sure that the observed shifting of the ellipsometry signal is definitely caused by the cryostat
6.2 Wetting Investigations on Silicon

Figure 6.15: A real time snapshot of the change of the ellipsometer angle $\delta \Delta$ (and hence the film thickness) of a saturated liquid hydrogen film on silicon upon laser heating is shown. The temperature is about 14 K, slightly above $T_3$ of hydrogen. The thickness decreases (as $\delta \Delta$ decreases) when the heating laser is switched on, and recovers to the original value before heating when the heating laser is turned off.

Optical windows during temperature scanning, the same experiments were repeated a few times using an empty cell (Cooling and warming of the silicon). In Fig. 6.14 typical results of such investigations are shown. A major part of the signal drift should be ascribed to the birefringent effects of the optical windows on the polarized light.

It should be noted that neither the direction of shifting nor its magnitude are always the same. So there are other unknown factors which also cause shifting of the signal. These shifts can change from run to run. For instance, once the setup is warmed up (e.g. for mounting a new substrate) and cooled down again, it is quite difficult to create exactly the same conditions as before. Thus, making a correction by linearly subtracting the drifting effect from the measured values in order to get the real thickness of the film seems not to be reliable.

6.2.2 Differential Method

This problem of shifting the signal is overcome by applying a new differential method with which we are able to resolve the film thickness at different temperatures. This method relies on the desorption and adsorption of the film at a certain temperature by local heating of the substrate for a limited time. Thus from the reaction of the ellipsometry signal a difference, which is equal to the thickness of the adsorbed film, can be extracted.
Results and Discussion

Figure 6.16: Wetting behaviour of hydrogen on silicon measured with the differential method. $d$ is normalized to the thickness in saturation above $T_3$ of hydrogen. This is done for a convenient comparison of the resulted solid thickness far below triple-point of hydrogen and that on the gold substrate depicted in Fig. 6.4. The solid thickness has increased significantly as the silicon is smoother than gold substrate.

In addition to the ellipsometer probe laser with a power around 100 $\mu$W, (source (1) in Fig. 5.3), a heating laser with a power of about 10 mW, (laser (2) in Fig. 5.3), was focused onto the probe spot on the surface of the silicon substrate. This laser was periodically switched on and off at a frequency of 3.3 mHz. In the 'on'-state, the intensity of the heating laser is sufficient to desorb the major part of the adsorbed film except the 3 monolayers which appeared to be more strongly bound to the surface. In the 'off'-state, the film quickly recovers to its initial thickness without the heating laser, as shown in Fig. 6.15. The difference between 'on' and 'off' thus provides information, free of drift effects, about the film thickness (apart from the remaining strongly bound layer). To achieve the situation which is explained above, the heating process should be efficient. This was achieved by isolating the silicon wafer from the substrate holder, i.e., there was no direct thermal contact between the silicon and the body of the cell. However, it should be noted that the efficiency of the heating method is not the same at all temperatures, and the desorption of the film can be done more effectively at lower temperatures. This effect can be seen by plotting the increase of the substrate temperature upon heating at different ambient temperatures. At temperatures close to the $T_3$ of hydrogen the increase of the substrate temperature is about 0.14 K upon heating, whereas this amounts to 0.5 K at a temperature of about 10 K. By further lowering the temperature till, e.g., 4 K the rising temperature will reach even values of a few kelvin.

This effect should be ascribed to the state of the adsorbed material inside the cell since the only ways of heat dissipation from the substrate are through the ambient gas molecules and probably the adsorbed film itself. At higher temperatures, both the vapour pressure and the film thickness are quite significant such that both of them can considerably contribute into the mechanism of heat dissipation.
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Figure 6.17: Warming curve of Fig. 6.16 plotted on a logarithmic scale. In contrast to the case of hydrogen on gold (Fig. 6.5), the data deviate from the linear behaviour already at \( T = 13.51 \text{ K} \) \( (\log(t) = -1.5) \). This indicates the existence of a significant solid thickness which is not observed on gold. The slope of the straight line is \(-0.31\) which is in good agreement with the \("-1/3\"-power law very close to the triple-point.

transfer from the substrate into the ambient media. So at higher temperatures an equilibrium can be reached much faster. In contrast, at low enough temperatures both the vapour pressure and the film thickness are negligible which means creating a temperature gradient inside the cell can be done more effectively.

The data presented here are obtained with the differential method. The first experiments were done for the case of hydrogen on silicon (see Fig. 6.16). In the figure the thickness, normalized to the saturated thickness above the \( T_3 \) of hydrogen, is plotted versus temperature. This is mainly done for a convenient comparison between the solid thickness of hydrogen, well below \( T_3 \), on silicon with those resulted on the gold substrates. The thickness saturates below 13 K at a value of 0.32 in units normalized to the thickness above \( T_3 \) (which is 55 ± 5 Å), corresponding to 17.5 Å. Compared to the value on rough gold substrates \((d \approx 10 \text{ Å}, \text{Fig. 6.4})\) the thickness is thus significantly increased. This effect is illustrated in Fig. 6.17, which shows the film thickness on silicon in a logarithmic scale, such as in Fig. 6.5. Again a power law is observed with a value of \( \beta = 0.31 \pm 0.02 \), but in contrast to Fig. 6.5, the data display a clear deviation from this law for \( \log (t) > -1.60 \), where the thickness starts to saturate. This saturation at low temperatures can be interpreted as evidence for the solid hydrogen to form a distinctly thicker film on the smooth silicon substrate. The investigations of hydrogen on silicon were repeated many times both on the same and on different silicon substrates. The results which are presented above are reproducible on all silicon substrates with only small discrepancies\(^3\). The film always deviates from the linear behaviour at \( T \sim 13.5 \text{ K} \). The same

\(^3\)We have always used silicon substrates from the same supplier but it could be that the substrates were only slightly
Figure 6.18: Wetting behaviour of deuterium on silicon. The thickness $d$ is normalized to the one in saturation above $T_3$ of deuterium which allows a comparison with the results obtained for deuterium on gold illustrated in Fig. 6.6. An increase of the film thickness far below the triple-point can be seen. These data are analysed in the same way as those of hydrogen on silicon.

Experiments were performed for deuterium on silicon, and their results are shown in Fig. 6.18. For comparison purposes, the data are normalized to the thickness at saturated vapour pressure. Compared to the case of deuterium on gold (see Fig. 6.6), the solid thickness has indeed increased on silicon. This is in accord with the theoretical conclusion that a thicker solid film should form on silicon than gold. The only difference between Figs. 6.6 and 6.18 is the temperature range over which the data are plotted. For the case of deuterium on silicon, the measurements were done up to $T = 16.25 \text{ K}$. As can be seen from the data on gold (Figs. 6.6) below 16.25 K the changes in deuterium thickness are quite small.

In Fig. 6.19, the same data of deuterium on silicon (warming curve in Fig. 6.18) are plotted in a logarithmic scale. As shown, at temperatures very close to the $T_3$ of deuterium a power law behaviour is resulted. The straight line is a fit to the data which gives a value $\beta = 0.3 \pm 0.01$ for the exponent. The agreement with theoretical value "1/3" is very good. In this figure, at $T = 17.66 \text{ K}$ ($\log(t) \sim -1.2$) the deviation from the power law behaviour shows growth of a significant solid thickness on silicon.

To make a final statement on the wetting behaviour of deuterium and hydrogen on silicon, some more experiments may be needed. This is specially important for deuterium since the data obtained for deuterium are, although smooth in linear scales (Fig. 6.18), but noisy when plotted in logarithmic scales (Fig. 6.19). Furthermore, it is of particular importance to this work, e.g., to see which one of
deuterium and hydrogen saturates faster at low temperatures and whether there is any characteristic in the deviation form from the power law.

A partial evaporation of the liquid layer (at saturation above $T_3$) due to the heat transfer from the ellipsometry laser beam itself into the substrate may also occur. That would mean the film thickness under investigation should in principal be thinner than its real thickness without having the ellipsometry beam on it. Although that is a standard situation for all the physisorption experiments which conduct optical measurements, this effect can be reduced by decreasing the power of the ellipsometry laser. However, as mentioned before in our setup, a power of 100 $\mu$W is in principal necessary to achieve a measurable signal with a relative good signal to noise ratio on the photomultiplier.

### 6.2.3 Laser Cleaning and Annealing

The idea of laser cleaning is to remove unwanted contaminations, e.g. water, from the silicon surface. This occurs during mounting the substrate into the cell at room temperature or during cool down (we do not have ultra high vacuum conditions). For the cleaning procedure, we focus the light of a powerful laser diode (200 mW) on the same area of the substrate where the ellipsometry beam hits the surface. This is done at the beginning of the experiment, and the laser light is continuously left on while cooling the cell from room temperature down to the working temperature. In this way we can keep the temperature of the substrate about 30 K above the ambient temperature in the cell. The
Figure 6.20: Result of the laser annealing of silicon on the solid film thickness. Laser annealing is done at 9 K with hydrogen adsorbed on silicon. A significant increase of the solid thickness at this temperature is obvious. Thereafter cooling and warming are done and show that, after annealing, the film is always thicker than before. A slight increase of the thickness below 9 K should be ascribed to the efficiency of heating at lower temperatures (see the text for more explanation).

colder cell walls thus act as a trap for any material desorbed from the silicon substrate, and moreover prevent contamination of the sample surface during cool down. We found from other experiments that most of the usual contaminations of a cooled substrate surface can be considerably removed by this procedure. After reaching a low temperature (14.2 K), the cell was kept several hours under these conditions. Then the cleaning laser was switched off, and after establishing thermal equilibrium between the cell and the substrate, an adsorption isotherm of hydrogen was taken. In the next step, the cell was slowly cooled and warmed up between 9 K and 14 K. The observed $T_3$-wetting behaviour and determined solid hydrogen film thickness, however, was about the same as those measured on uncleaned silicon substrates (Fig. 6.16). This shows that standard contaminations of the silicon surface have no crucial influence on the wetting behaviour, in agreement with the experiments which are done on the surface of the gold.

After the second cooling, the temperature was fixed at 9 K, and the laser annealing procedure, using the ruby-laser setup (laser (3) in Fig. 5.3) was performed. After annealing the silicon substrate the hydrogen film thickness increased by about two monolayers. Then we varied the temperature between 3.5 K and 14 K. The overall thickness in this temperature range, where only the solid film is present, became indeed somewhat larger. Yet, the typical $T_3$-wetting behaviour was observed, i.e., incomplete wetting of the solid hydrogen film. The result of these experiments are shown in Fig. 6.20. At the end of the experiment, the surface quality of the silicon was analysed by SEM. No signs of laser-induced damages were seen on the area where the measurements were done.
Although we observed only a small increase in the thickness of the solid film, this result is promising and in qualitative agreement with the calculations of Esztermann et al. [Esz02]. Clearly more experiments are needed to check the influence of surface roughness on the growth of a solid hydrogen film and to compare more quantitatively with the theory. For that it is necessary not only to manipulate the surface of the substrate, but also to characterize this surface on the atomic scale.
We have investigated the triple-point wetting of, in particular, hydrogen and deuterium films physisorbed on the surface of gold and silicon substrates. Triple-point wetting behaviour was observed for all the systems which were investigated. Wetting by the liquid adsorbate occurred, and the dewetting followed as the system left the liquid-gas coexistence. In the dewetting state, only a few monolayers of the solid adsorbate existed on the surface. A comparison between the experimental results and the theoretical prediction of the GS-theory [Git84] revealed some discrepancies. In contrast to the theory, which predicts different wetting behaviours depending on the value of the substrate strength, a universal dewetting behaviour was observed for all adsorbates.

Mixtures of hydrogen-deuterium were studied. This was motivated by the fact that different properties between deuterium and hydrogen would change the wetting behaviour of the system. For different mixing ratios, an effective triple-point was defined which fell always between the triple-points of pure hydrogen and deuterium. However, the solid film thickness at temperatures far below the triple-point remained unchanged. No sign of phase separation was observed in hydrogen-deuterium mixed systems. The pronounced hysteresis which appeared between cooling and heating paths was understood with the help of the phase diagram of binary systems. The hysteretic behaviour also implied that the species concentrations were not the same in different phase states. In our experiments the concentration of the species in the gas phase was determined from the measured vapour pressure using the partial vapour pressure relationship at a certain temperature.

Preparing a smoother gold surface did not affect the wetting behaviour of hydrogen. Although the AFM analysis showed a distinctly smoother gold surface prepared on silicon, further investigations revealed that, in the microscopic scale, the roughness had the same characteristics. Investigations on the surface of silicon wafer showed the usual triple-point wetting behaviour for both hydrogen and deuterium. A steeper film growth of hydrogen and deuterium was observed close to the triple-point. Further analysis of data on silicon pointed to a clear deviation from the "1/3"-power law at temperatures far below the triple-point. We believe that this is a clear sign of a significant solid layer growing on a silicon wafer. We also studied the in situ annealing of a silicon wafer. In spite of technical difficulties, on annealed silicon, the thickness of solid hydrogen film indicated an increase of two to three monolayers.

Our results exhibit that the effect of the surface quality of the substrate on the wetting phenomenon is decisive and should be further investigated. Based on our findings, there are quite a series of experiments that can be carried out. In order to obtain complete wetting by solid hydrogen on a solid substrate, the role of the substrate roughness on wetting must be understood. Preparing smoother and cleaner substrates is important and the results of silicon annealing suggest that in situ annealing of silicon should be done more extensively. In addition, smoother gold substrates may be prepared using methods other than thermal evaporation. Using ellipsometry also allows applying other well-defined substrates such as graphite. At the same time, it would be interesting to study the substrates which have different micro-roughness profiles. This may already provide us with more insight about
the effect of roughness on wetting phenomenon. Finally, experiments such as preplating can be repeated after the effects of substrate roughness are studied thoroughly.
In this work, the triple-point wetting of molecular hydrogen isotopes and other noble adsorbates was investigated. In the experiments, hydrogen was used mainly as a model system on the surfaces of gold and silicon. The gold substrates were evaporated thin films on polished glass whereas the silicon substrates were cut from commercial silicon wafers.

The motivation for the research was the prediction of the GS-theory [Git84] that complete or incomplete wetting of a substrate by an adsorbate occurs, depending on the relative substrate strength. The strain induced into the adsorbed solid film, is due to the lattice mismatch between substrate and adsorbed film. However, some discrepancies were observed between the experimental findings and the theoretical prediction. For instance, incomplete wetting of solid hydrogen film on gold occurred, whereas GS-theory predicts nearly complete wetting. This means that other factors should also play a role in the dewetting phenomenon of hydrogen. In the GS-theory, the substrate is assumed to have a well defined surface. In reality, of course, any substrate surface has a finite roughness profile. This effect is considered in an elaborate theory by Esztermann et al. [Esz02] which showed that dewetting can be promoted by the finite roughness of the substrate underneath. This theory is in good agreement with our experimental data. The important conclusion is that a finite roughness always enforces triple-point wetting and the described scenario plays the decisive role for any wetting situation where solid layers are involved.

The GS-theory was then investigated by using surface plasmon spectroscopy on the surface of gold substrates. The usual effect of triple-point wetting was always observed for hydrogen, deuterium, methane and argon. Thereafter it was tried to change the interaction of hydrogen molecules and gold atoms via preplating. According to the GS-theory, argon and methane are adequate preplating materials. However, preplating with argon and methane showed no significant effect in the wetting behaviour of hydrogen. Preplating with deuterium also had no effect on the wetting behaviour of hydrogen either, instead a mixing of hydrogen and deuterium occurred.

For the hydrogen-deuterium mixed systems, the wetting occurred at an effective triple-point temperature which, depending on the species concentration, fell always between the $T_3$'s of pure hydrogen and pure deuterium. The effective triple-point showed a clear dependency on species concentration of the mixture. In contrast to pure systems, the onset temperatures were different for cooling and heating paths and a hysteresis resulted. The hysteretic behaviour in the mixed systems was attributed to the different species concentrations in the solid, liquid and gas phases. To figure out a complete phase diagram of hydrogen-deuterium mixture a few more experiments should be done.

Preparing a smoother gold substrate was encouraged by the theory of Esztermann et al. [Esz02]. This was done, in a novel way, by evaporating gold on a silicon wafer and then by bringing it back onto the prism. In spite of all efforts, no significant change was observed in the wetting behaviour of solid hydrogen. Thereafter, the gold surfaces, prepared on silicon and on glass substrates, were analysed.
by AFM. Although, on the nanometer scale, the surface of the gold prepared on silicon seemed to be smoother than the one prepared on glass, further investigations by Esztermann showed that, on the micrometer scale, both substrates have essentially the same roughness profile. The important result is that the micro-roughness plays the dominating role in the wetting of solid hydrogen. This required smoother surfaces such as silicon wafer.

On silicon surfaces, the investigations were done using null ellipsometry spectroscopy. The silicon surface was about one order of magnitude smoother than the gold film. Although, on silicon surface, the usual wetting behaviour of hydrogen occurred, a clear difference in the thickness of the solid film was observed. Below $T_3$ the behaviour of liquid hydrogen follows a "1/3"-power law. This was always observed on gold surfaces. On silicon, however, a deviation from this behaviour occurred which means that, at some point, the film saturated and upon a further decrease in temperature, the solid thickness became significant. At $T \ll T_3$, a comparison between hydrogen thicknesses on gold and silicon showed an increase of, at least, 3 solid monolayers on silicon. This is a clear evidence that surface roughness governs the wetting behaviour of solid hydrogen. For deuterium on silicon the same results were obtained which was another confirmation for that effect.

*In situ* laser annealing of silicon was also performed. The annealing was done by using a nanosecond pulsed ruby laser. Upon annealing, the melting and recrystallization of the silicon in a very short time occurred. This allowed us to get rid of the dirt and have a well defined silicon surface. Compared to an unannealed silicon wafer, a further increase of about two monolayers of solid hydrogen was achieved on an annealed silicon surface.

Our results show that the surface roughness profile dominates the wetting of solid adsorbate. Further investigations should be carried out to reach a near ideal surface.
Zusammenfassung


Die Ergebnisse, die im Rahmen dieser Arbeit gewonnen wurden, bekräftigen die Voraussagen der Theorie. Sie zeigen weiterhin, dass eine vollständige Benetzung des festen Wasserstofffilms realisiert werden kann, wenn die Substratrauigkeit weiter verkleinert wird.
Bibliography


BIBLIOGRAPHY


[Hea55] Heavens, O. S.: *Optical properties of thin solid films*. Butterworths Scientific Publica-

[HeC94] Hecht, D. and D. Stark: *Electrical and structural properties of thin gold films on glas


[Her89] Herminghaus, S. and P. Leiderer: *Improved attenuated total reflectance technique


[Hey87] Heyraud, J. C. and J. J. Metois: *Equilibrium shape of an ionic crystal in equilibrium

[Hil49] Hill, T. L.: *Statistical mechanics of adsorption. V. thermodynamics and heat of adsorp-

(1984). 6, 21


[Ita91] Itakura, A. and I. Arakawa: *Ellipsometric study of Xe physisorbed on Ag(111) and

reflectivity measurements on silicon and germanium using a pulsed excimer KrF laser

[Kar90] Kardar, M. and J. O. Indekeu: *Adsorption and wetting transitions on rough sub-

R. Howe (Herausgeber): *Chemistry and physics of solid surfaces VII*, Page 65. Springer,


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Appendices
Appendix A

Linear Approximation Theory

A.1 Linear Approximation Method

In this section, we introduce explicitly the two equations for the thickness coefficients which were already used in section 4.2.4. These linear equations are given by

\[ \Delta = \bar{\Delta} - \eta d , \]  
\[ \psi = \bar{\psi} + \gamma d . \]

Here, \( \eta \) and \( \gamma \) are defined as:

\[ \eta = \frac{4\pi \cos \phi_0 \sin^2 \phi_0 (n_1^2 - 1) \left( \frac{1}{n_1^2} - a \right) \left[ \cos^2 \phi_0 - a + \sin^2 \phi_0 (a^2 - \dot{a}^2) \right] + \dot{a}^2 (1 - 2a \sin^2 \phi_0) \lambda \left[ \cos^2 \phi_0 - a + \sin^2 \phi_0 (a^2 - \dot{a}^2) \right]^2 + \dot{a}^2 (1 - 2a \sin^2 \phi_0)^2}{\lambda \left[ \cos^2 \phi_0 - a + \sin^2 \phi_0 (a^2 - \dot{a}^2) \right]^2 + \dot{a}^2 (1 - 2a \sin^2 \phi_0)^2} \]  
\[ \]  
and

\[ \gamma = \frac{2\pi \sin 2\bar{\psi} \cos \phi_0 \sin^2 \phi_0 (n_1^2 - 1) \dot{a} \left( \frac{1}{n_1^2} - a \right) (1 - 2a \sin^2 \phi_0) - \left[ \cos^2 \phi_0 - a + \sin^2 \phi_0 (a^2 - \dot{a}^2) \right] \lambda \left[ \cos^2 \phi_0 - a + \sin^2 \phi_0 (a^2 - \dot{a}^2) \right]^2 + \dot{a}^2 (1 - 2a \sin^2 \phi_0)^2}{\lambda \left[ \cos^2 \phi_0 - a + \sin^2 \phi_0 (a^2 - \dot{a}^2) \right]^2 + \dot{a}^2 (1 - 2a \sin^2 \phi_0)^2} . \]

The quantities \( a \) and \( \dot{a} \) are:

\[ a = \frac{n_2^2 - k_2^2}{(n_2^2 + k_2^2)^2} \]  
\[ \]  
and

\[ \dot{a} = \frac{2n_2 k_2}{(n_2^2 + k_2^2)^2} . \]
$n_2$ and $k_2$ are the real and imaginary parts of the complex index of refraction of the substrate ($\tilde{n}_2 = n_2 - ik_2$). All the other parameters are defined with respect to Fig. 4.4.

These two formulas are solved using Mathematica to give the correct values for the condition of the experiment (see section 4.2.4).
Appendix B

Selection of the Grand Canonical Potential

The excess surface free energy $\Sigma$ is defined as the ratio of the grand canonical potential $\Omega$ and surface $A$, $\Sigma = \Delta\Omega/A$, in which $\Omega$ is defined with respect to a reference system. The reference system in this case is a nonwetting state. In this section, the explicit form of $\Omega$ from a more microscopic view is introduced.

B.1 Density Functional Theory

It can be shown that, for a system with a density distribution $\rho(r)$, an external potential $V(r)$ can be found [Mer65]. Since the grand canonical potential $\Omega$ is a function of external potential, there should exist a functional $\Omega[\rho(r)]$ which can be physically minimized for a proper density distribution.

In general, the functional form of $\Omega$ is not precisely known, and some approximations must be used. The two simplest approximations which may be applied are local-density-approximation (LDA) and LDA with mean-field-theory (MFT). In both of the approximations the aim is to find a simpler form of $\rho(r)$. Having an adequate functional form is enough to look for a minimum by a variational calculation from which reasonable $\rho$ and $\Omega$ can be derived.

In chapter 3, we considered the grand canonical potential as a sum of three terms:

$$\Omega_{total} = \Omega_{Thrm.} + \Omega_{GS} + \Omega_{C} \quad (B.1)$$

Here we are interested in some more details of the thermodynamic term $\Omega_{Thrm.}$. The $\Omega_{GS}$ is the term which has been calculated by Gittes and Schick [Git84], necessary for the distortion of the solid adsorbate by the potential of the substrate. The $\Omega_{C}$ is responsible for the bending of the film by the substrate roughness of the substrate which has already been discussed.

The $\Omega_{Thrm.}$ can be split into three terms:

$$\Omega_{Thrm.} = \Omega_{f} + \Omega_{V} + \Omega_{\phi} \quad (B.2)$$
where $\Omega_f$ is the free energy density of a homogeneous system which can be written in the following form

$$\Omega_f(T, [\rho]) = \int f(T, \rho(r)) - \frac{1}{2} \rho^2(r) \int_{-\infty}^{+\infty} \omega(|z|) d|z| d^3r$$

(B.3)

and

$$\omega(z) = \int_{0}^{2\pi} \int_{0}^{\infty} \phi \left( \sqrt{r^2 + z^2} \right) r dr d\phi$$

(B.4)

where $\phi(r)$ is the long-range, attractive part of the Lennard-Jones potential.

$$\phi(r) = -4\epsilon \left( \frac{\sigma}{r} \right)^6$$

(B.5)

The term $\Omega_V$ is the grand canonical potential resulted from the van der Waals interaction:

$$\Omega_V(\mu, [\rho]) = \int (V(z) - \mu) \rho(r) d^3r$$

(B.6)

$\Omega_\phi$ is the mean-field-energy of the long-range attraction part of the Lennard-Jones potential:

$$\Omega_\phi[\rho] = \frac{1}{2} \int \int \phi(|r_1 - r_2|) \rho(r_1) \rho(r_2) d^3r_1 d^3r_2$$

(B.7)

### B.2 Sharp-Kink Approximation

In addition to grand canonical potential the form of density distribution should be defined. This is done based on the *sharp-kink approximation* (shown in Fig. B.1) which can be written as

$$\rho(r) = \rho(z) = \begin{cases} 
\rho_s & d_W < z < l_s \\
\rho_l & l_s < z < l_s + l_l \\
\rho_g & l_s + l_l < z < L \\
0 & \text{other}
\end{cases}$$

(B.8)

In the reference system, nonwetting should take place, that is:

$$\rho_{ref}(r) \equiv \rho(z) = \begin{cases} 
\rho_g & d_W < z < L \\
0 & \text{other}
\end{cases}$$

(B.9)
where \( d_W (d_W \ll l_s) \) and \( L (l_l \ll L) \) are both microscopic but finite distances. \( L \) is the size of the system. \( \rho_g, \rho_l \) and \( \rho_s \) are the bulk gas, liquid and solid densities. In the calculation, these densities are constants, and only \( l_l \) and \( l_s \) are variables. Consequently, the grand canonical potential functional \( \Omega[\rho] \) will now be dependent only on \( l_l \) and \( l_s \), i.e., \( \Omega(\rho) = \Omega(l_l, l_s) \). The rest of the calculation, which was partly presented in section 3, should be done numerically.

**Figure B.1:** Illustrated are the sharp-kink-approximation (dashed line) and the physical (solid line) density variation of an adsorbed film near a surface.

There are in fact some assumptions behind the approximation used, and may be noticed.

The sharp-kink approximation assumes that the different bulk phases have a layering structure on the substrate. Thus, it is to be expected that the expansion of the interface in the \( z \)-direction is not equal to zero, but its order of magnitude is of the order of correlation length.

This approximation is therefore adequate for thick layers far from critical point, while for thin layers which only contain a few monolayers, the approximation loses its validity.

The microscopic density of the solid, which is strongly inhomogeneous because of the lattice structure, is substituted by its average value \( \rho_s \). This approximation is valid for external potentials, which are only slowly varying on the length scale of the lattice constant of the condensed phase.

Moreover, substrate roughness is totally ignored by assuming translational symmetry in the \( x \)- and \( y \)-direction. The effect of roughness is separately considered as an extra term \( (\Omega_C) \) in free energy which is already discussed. Finally, this approximation is adequate for surfaces with weak curvature (weak roughness amplitude).
Appendix C

Plasmon Resonance-Width

Besides measuring the film thickness, applying surface plasmon spectroscopy also allows one to gain some other information about an adsorbed film. Here, we briefly demonstrate how the width of the plasmon curve proceeds as the film grows.

The overall shape of the resonance depends on some parameters which were discussed in chapter 4. For a certain substrate, e.g. gold, the width of the resonance is mainly determined by surface roughness. As pointed out (see, e.g., [Rae86]) on a rough surface, damping the surface plasmons is done much faster. This, in turn, leads to the broadening of resonance width. Thus by plotting the width of the resonance one can gain some information about the film surface. In the experiment this was realized by using lock-in technique. The lock-in amplifier was driven at a frequency which was a factor of two larger than the resonance frequency. Under these conditions, the output signal is equal to the curvature of plasmon curve at the resonance. This is inversely proportional to the resonance-width (see Fig. 5.2). In Fig. C.1 the curvature of the resonance (open circles) and the thickness (solid squares) of an adsorbed hydrogen film versus reduced pressure are plotted. The 2f-signal has an approximately constant value in the nonsaturated region, whereas it drops steeply as the system approaches saturation. This means, the resonance-width is significantly broadened in the thick film regime. Under these circumstances, the film should have a rough surface.

In Fig. C.2, the solid and dotted curves are again a measure of the surface roughness of hydrogen (left figure) and deuterium (right figure) films at different temperatures. The solid and dotted curves in these figures are proportional to the inverse of the resonance-width for cooling and heating runs, respectively.

Figure C.1: The changes in the width of the resonance (open circles) versus reduced pressure are shown. The solid squares are the thickness. The 2f values are inversely proportional to the resonance width. As the saturation is approached the signal drops steeply which shows increasing the plasmon width.
Figure C.2: Process of the resonance-width versus temperature is demonstrated. The left and the right plots are the data of hydrogen and deuterium, respectively. As can be seen the same effect is observed irrespective of the kind of material. That means the resonance-width broadens as the wetting regime approaches. This, in turn, signifies that the surface of the film becomes rough near $T_3$ of the adsorbate.

This that capillary waves exist on the surface of thick liquid film has theoretically been predicted some time ago and proved by a number of experiments. Here, it was meant to show another capability of surface plasmon spectroscopy. In fact, more information on the dynamic of the adsorbed film can be obtained if the response of the resonance is analysed further.
Acknowledgments

I am grateful to Prof. Dr. Paul Leiderer for the support and the guidance he has provided throughout my research. I have learned a lot from him and benefited from many stimulating discussions and suggestions.

I would like to thank Dr. Jürgen Klier both for the hints and his support in and out of the laboratory. Our discussions made my understanding of wetting phenomena more complete.

I would like to thank Prof. Dr. Hartmut Löwen and Ansgar Esztermann from Düsseldorf. I have enjoyed fruitful and very pleasant collaborations with them. This helped to particular success of the work.

Stefan Tibus and Jörg Angrik took part in development of the experimental setup and partly participated in doing measurements. I am really thankful to them.

Appreciation is also expressed for the excellent technical aids and supports from Louic Kukk and Christoph Goldbach. I also appreciate technical supports from Wolfgang Betz in the early stages of the work.

I am also thankful to the helium liquefaction team and the workshops of the University of Konstanz for assistant in building up facilities in laboratory and experimental setups.

Further on, I wish to thank:

Andreas Würl, Konrad Mangold, Jörg Zimmermann and Spyros Koutsoumpous for the fantastic and pleasant time both in and outside the University. Jörg also corrected the manuscript. It was great to be with them.

Ismail Karakurt for correcting the major part of the manuscript.

Artur Erbe for his guidance during preparation of defense exam.

Former and present members of Lehrstuhl Leiderer, in particular those who supported this work by allowing use of their devices and provided a pleasant time during coffee breaks and other occasions.

I would also like to acknowledge the financial assistant from Deutsche Forschungsgemeinschaft.

At last, but by no mean at least, I would specially like to thank my family. They have supported and encouraged me throughout my life. This is for them!