Annealing behavior of quench-condensed hydrogen and deuterium films

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We have studied the annealing behavior of thin molecular hydrogen and deuterium films (typical thickness 10 nm) prepared by quench-condensation at 1.5 K on a silver substrate. Changes in the optical thickness and the heterogeneity of the films were monitored using optically excited surface plasmons. Upon annealing the films exhibit an irreversible change from a homogeneous to a strongly heterogeneous structure on a length scale of some hundred nm, accompanied by an apparent loss in optical thickness. This behavior is interpreted as being due to the formation of large bulk crystallites on the surface, resulting from the incomplete wetting of solid hydrogen on silver.

1. Introduction

The properties of quench-condensed films have been a topic attracting increasing attention over the past years. Their structure and excitations may differ considerably from films in thermal equilibrium. Atoms and molecules exhibiting simple van der Waals-type intermolecular interaction, like rare gases and the hydrogen isotopes, have been used as models to study the properties of these systems, using phonon scattering [1], X-ray diffraction [2], surface state electrons [3] and heat capacity measurements [2,4]. Generally the films are found to be strongly disordered.

We have employed a new technique using optically excited surface plasmons to study how the relaxation towards the thermodynamic equilibrium in these films proceeds upon thermal annealing.

2. Experimental

Surface plasmons (SP) are optically excited on a thin silver film using the Kretschmann configuration [5]. The silver, serving also as substrate for

the quench-condensation, is thermally evaporated onto the base of a glass prism. We illuminate the silver film from the glass side with a HeNe-laser incident at a particular angle Θ_R , where the surface plasmons are resonantly excited. This leads to a sharp drop in the totally reflected light intensity at this resonance angle. Depositing a thin dielectric layer on the silver surface changes the SP resonance condition. The resulting shift in Θ_R is a measure for the optical thickness of the dielectric material.

Fig. 1 shows a calculation of Θ_R versus the optical thickness d of a H_2 -layer deposited on silver (using a refractive index of $\epsilon_{H_2} = 1.295$, i.e. assuming bulk density). Up to about $d = 1000$ Å the shift in Θ_R is in good approximation proportional to the layer thickness. Towards larger values of d it gets less sensitive due to the exponential decay of the SP field into the adjacent half-space. By accurately monitoring the shift in resonance angle we can thus directly measure the optical thickness of thin films deposited on the silver surface carrying the SP wave. In addition, we simultaneously determine the halfwidth in angle $\Delta\Theta$ of the SP resonance, which increases when the SP wave scatters from inhomogeneities

Fig. 1. Calculated surface plasmon resonance angle Θ_R on silver versus thickness of an additionally deposited H_2 -film (bulk density is assumed).

Fig. 2. Annealing behavior of a quench-condensed H_2 -film. The thickness d (solid line) is calculated using the relation in fig. 1. The dashed curve shows the simultaneously measured width of the surface plasmon resonance $\Delta\Theta$, normalized to the value on bare silver $\Delta\Theta(0)$. T is the annealing temperature.

in the film. Hence this provides a measure for structural changes within the dielectric film. Details of the measuring technique are described elsewhere [6].

The hydrogen films were quench-condensed onto the surface at ~ 1.5 K; the temperature of the gas entering the experimental cell was below 25 K. A low temperature of the incoming gas is crucial for the formation of disordered quench-condensed films [7]. We annealed the films at a rate of 0.5 K/h for the experiments shown below. Measurements at slower rates proved the results to be qualitatively independent of the annealing rate. The films were not in equilibrium with the vapor, since cold surfaces close to the prism in the experimental cell acted as cryopumps for desorbing gas molecules.

3. Results

Fig. 2 shows the results of an annealing experiment on a quench-condensed H_2 -film of ~ 100 Å thickness. The shift in Θ_R (plotted as optical thickness d , assuming bulk density) and the resonance width $\Delta\Theta$ (normalized to the value on bare silver) are plotted versus the annealing temperature. The film is initially homogeneous on a length scale of the order of the light wavelength, since the plasmon resonance width is not significantly

different from the value of the bare silver substrate. Between 2.5 and 3 K, however, there is a strong increase in SP scattering, accompanied by a drastic shift of d to about half its initial value. This state then prevails until the desorption of the hydrogen molecules sets in (slightly below 4 K). The annealing effect is a function of film thickness, being less pronounced for thin films than for thick films (the relative decrease in d for a film of 35 Å amounts to only $\sim 20\%$). All changes in d and $\Delta\Theta$ induced by the annealing are irreversible. Interrupting the annealing process at any point and subsequently lowering the

Fig. 3. Annealing behavior of a quench-condensed D_2 -film.

Fig. 4. Annealing behavior of a quench-condensed neon film.

temperature freezes in the particular state reached until then.

Quench-condensed HD and D₂-films exhibit the same behavior upon annealing. However, the temperature where the transition to the state exhibiting stronger SP scattering occurs, as well as the desorption temperature are shifted to higher values with increasing molecular mass, as shown for the case of deuterium in fig. 3. Also d continues to slightly decrease until desorption sets in.

In contrast to these findings, annealing of quench-condensed *neon* films does not lead to any significant changes in d or $\Delta\theta$ below the desorption temperature (see fig. 4).

4. Discussion

The crucial point in interpreting the observed annealing behavior is the pronounced decrease in d . This can be caused by either a real loss in coverage or by a drastic rearrangement of the molecules in the film, that would position a substantial number of them at a distance from the silver surface, where θ_R is not a linear function of the film thickness anymore (cf. fig. 1). A substantial coverage loss seems rather unlikely at temperatures well below the bulk desorption threshold. Also it would not be easy to see, why it should strongly depend on the initial film thickness.

We thus argue that our observations are a consequence of the wetting properties of hydrogen on silver. Migone et al. [8] have shown that hydrogen physisorbed on silver exhibits triple-point wetting, i.e., the thermodynamic equilibrium state of the system at low temperatures consists of an adsorbed film with a thickness of only one or two monolayers in coexistence with bulk crystallites. In order to minimize the energy, the crystallites should cover as little surface as possible, hence they might grow rather large. Recent experiments on dewetting of thin polymer films prepared off equilibrium by Reiter [9], who could observe the resulting equilibrium configuration by microscopy, showed similar results. The films collapsed into droplets, whose size scaled with the initial film thickness, exceeding it by about two orders of magnitude. In our case, for the film shown in fig. 2 the formation of crystallites with a size of ~ 4000 Å could lead to the observed apparent decrease in d . The presence of crystallites with sizes on the order of the light wavelength would also explain the strong scattering of the SP waves. The dependence of the effects on the initial coverage is in this picture simply a consequence of the increasing deviation from the linear dependence of θ_R on film thickness (cf. fig. 1).

It is quite surprising, though, that the mobility of the hydrogen molecules in the solid phase at temperatures of only a fraction of the triple point temperature seems to be large enough to facilitate such a drastic rearrangement. Since bulk diffusion should be negligible at these temperatures [10], diffusion at the surface appears as the only possible mechanism. In this context we mention a recent quasielastic neutron scattering measurement by Maruyama et al. [11], who probed surface mobilities of HD on MgO substrates in order to look for surface melting effects. They found that at a temperature as low as 7 K a fraction of $\sim 20\%$ of the top layer of a five monolayer thick film still shows liquid-like behavior with the according high diffusion coefficient. This fraction is expected to get even larger with increasing film thickness. Surface melting may thus be the origin for a high mobility of molecules at the surface even at rather low temperatures.

It remains unclear, why we do not see annealing effects in the quench-condensed neon films, which also exhibit triple point wetting on silver [12]. Possibly the surface diffusion on neon is not fast enough at temperatures below the desorption threshold.

5. Conclusion

We have investigated the annealing behavior of thin quench-condensed films of the hydrogens by monitoring the resonance angle of optically excited surface plasmons and their resonance width as measures for the optical film thickness and heterogeneity. Upon annealing the initially homogeneous films exhibit a transition to a state which is strongly heterogeneous on the scale of the light wavelength, accompanied by a pronounced decrease in resonance angle. The observations can be consistently explained by a dewetting process involving the formation of large bulk crystallites on a thin wetting film of monolayer thickness. The rearrangement of the molecules involved can only occur via surface diffusion. Recent measurements [11] indicate that surface melting might be the mechanism leading to the high mobilities necessary.

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References

- [1] T. Klitsner and R.O. Pohl, *Phys. Rev. B* 34 (1986) 6045.
- [2] N. Steinmetz, H. Menges, J. Dutzi, H. v. Löhneysen and W. Goldacker, *Phys. Rev. B* 39 (1989) 2838.
- [3] K. Kono, U. Albrecht and P. Leiderer, *J. Low Temp. Phys.* 82 (1991) 279.
- [4] R.B. Phelps, J.T. Birmingham and P.L. Richards, to be published.
- [5] E. Kretschmann and H. Raether, *Z. Naturforsch.* 23a (1968) 2135.
- [6] U. Albrecht, H. Dilger, P. Evers and P. Leiderer, in: *Process Module Metrology, Control and Clustering*, Eds. C.J. Davis, I.P. Herman and T.R. Turner, *Proc. SPIE* 1594 (1992) 344.
- [7] K.H. Müller, *Surf. Sci.* 184 (1987) L375.
- [8] A.D. Migone, A. Hoffmann, J.G. Dash and O.E. Vilches, *Phys. Rev. B* 37 (1988) 5440.
- [9] G. Reiter, *Phys. Rev. Lett.* 68 (1992) 75.
- [10] I.F. Silvera, *Rev. Mod. Phys.* 52 (1980) 393.
- [11] M. Maruyama, M. Bienfait, F.C. Liu, Y.M. Liu, O.E. Vilches and R. Rieutord, *Phys. Rev. Lett.*, to be published.
- [12] A.D. Migone, J.G. Dash, M. Schick and O.E. Vilches, *Phys. Rev. B* 34 (1986) 6322.