

High resolution surface plasmon measurements –
a sensitive probe for thickness and structural information of ultrathin films

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ABSTRACT

We describe the use of optically excited surface plasmons to measure the thickness of ultrathin films deposited on gold and silver surfaces with submonolayer resolution. Additional structural information on the film is obtained by looking at the scattering of the surface plasmons. Applications of this method to physisorbed and quench-condensed molecular hydrogen films and to spreading of liquids are presented.

1. INTRODUCTION

Since the first demonstration of optical excitation of surface plasmons (SP) by Otto¹ they have been widely employed for measurements of roughness², growth³ and optical constants⁴ of metal films, as well as for use as chemical or biological sensors. However, there have been rather few studies⁵ on very thin films. In this paper we demonstrate that optically excited SP measurements are very well suited for high resolution measurements of such films. They provide a sensitivity comparable with ellipsometric measurements, giving additional structural information via their scattering from interface inhomogeneities. In the following we will describe the basic setup for thin film measurements with SP. We will then show experimental results on physisorbed and quench-condensed molecular hydrogen films, and on profiles of molecularly thin PDMS drops, where scanning provides lateral resolution.

2. METHODOLOGICAL

The magnitude of the SP wave vector propagating along a metal-dielectric interface is greater than the wave vector of light in the dielectric, thus light incident on the interface cannot directly couple to the SP. Coupling can be achieved by using the evanescent wave resulting at total internal reflection in a prism with a refractive index higher than that of the dielectric. We employ the Kretschmann configuration⁶ where the evanescent wave penetrates through a thin metal film grown onto the prism base. The SP is then excited at the interface between the metal film surface and the adjacent medium, if the projection onto the surface of the photon wave vector in the evanescent wave, given by the incidence angle, matches the wave vector of the SP. At this resonance angle Θ_{res} a sharp resonance dip is observed in the reflected light intensity (see insert in fig.1).

Condensing a thin dielectric film onto the metal surface increases the dielectric constant of the adjacent medium seen by the SP, leading to a shift of Θ_{res} towards larger angles. Typical values for the shift on silver are $\Delta\Theta_{res} = 10^{-2} \text{deg}/\text{\AA} \cdot (\epsilon - 1)d$ for a dielectric film of thickness d with a dielectric constant ϵ . This proportionality holds for films thin compared to the penetration depth of the SP, which is on the order of the wavelength. Exact values are calculated using Fresnel's equations. We can thus accurately measure optical thicknesses of dielectric films on metallic surfaces (provided the dielectric constant is known). Since the SP field is localized to the interface, they scatter very effectively from inhomogeneities in the film. Hence changes in the scattering give information about structural changes within the film.

The method is not really restricted to metal surfaces. In fact any dielectric that can be prepared as a thin film or a thin slab can be used as a substrate exploiting the coupling of the SP to waveguide modes in the dielectric⁷.

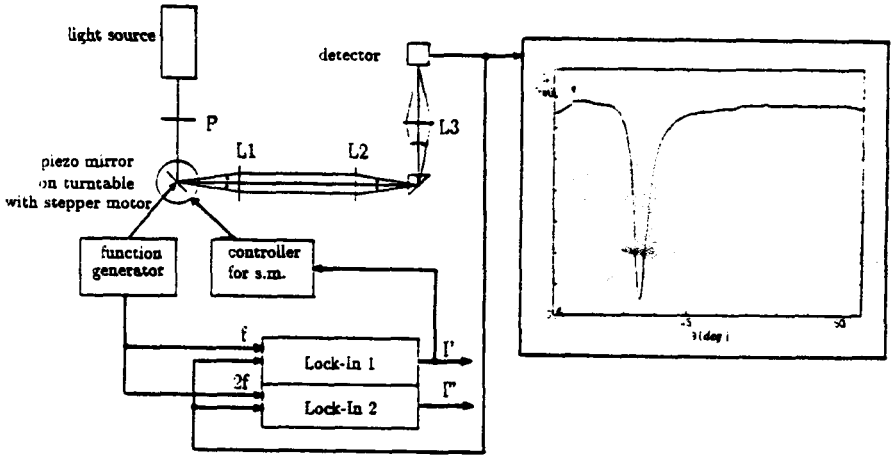


Figure 1: Schematic experimental setup; L: Lenses, P: Polarizer. The insert shows the surface plasma resonance in the reflected intensity vs. incidence angle on Ag, the arrow denoting the critical angle for total internal reflection

3. EXPERIMENTAL

The basic experimental setup used in our experiments is shown in fig.1. Parallel light from a monochromatic source (the experiments described below were all done with HeNe-lasers) is p-polarized and reflected from a mirror mounted on a bimorph piezo vibrating at a frequency of around 1 kHz. The mirror is mounted on a motor-driven turntable for angular adjustment. From there it passes through a couple of lenses (L1 and L2) in a telescope setup onto the prism base, hitting it parallel at a fixed point at sinusoidally varying incidence angle, and is then detected. This angular modulation about the resonance angle (modulation amplitudes are small compared to the resonance width) allows us to use Lock-in detection of changes in the SP resonance condition. The Lock-In amplifier 1 operated at the driving frequency f of the piezoelectric mirror gives a signal proportional to the angular derivative of the reflected intensity $dI_r(\Theta)/d\Theta$, measuring changes in Θ_{res} . This signal can also be used to keep the angle of incidence always at resonance by feeding it to the motor control driving the turntable. Lock-In amplifier 2 operates at $2f$ giving the second derivative $d^2I_r(\Theta)/d\Theta^2$ which at Θ_{res} equals the curvature at the resonance minimum and is inversely proportional to the width of the resonance $\Theta_{1/2}$. With our experimental setup we are able to detect shifts in Θ_{res} of less than 10^{-3} degrees and changes in $\Theta_{1/2}$ better than 1%. The resolution is limited by the mechanical stability of the optical arrangement and by the detection noise of the reflected light intensity. Part of the experiments described below are performed at low temperatures, the prism being mounted in an optical cryostat. Since SP decay chiefly to phonons, at lower temperatures we have to work with attenuated light in order to keep heating of the illuminated area negligible (below 1 mK in our case), resulting in increased noise at the detector. Care has also to be taken to avoid interferences at

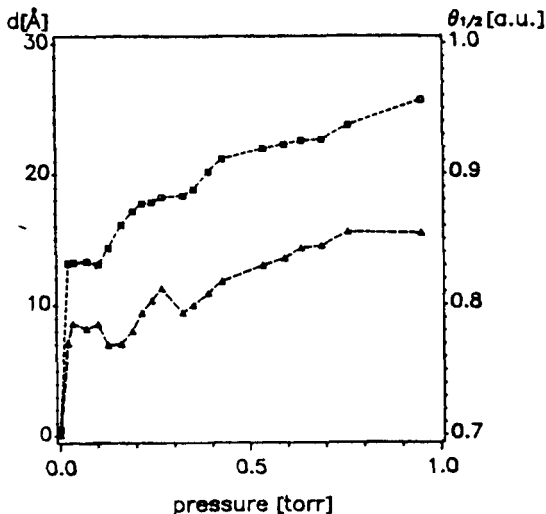


Figure 2: Adsorption isotherm of molecular hydrogen on gold: equilibrium film thickness vs. pressure (squares) and the corresponding SP width (triangles).

the optical components in order not to obscure features in the $\Theta_{1/2}$ signal with intensity changes caused by interference.

We present measurements on silver and gold which show very sharp SP resonances. The metals were thermally evaporated onto the prism base (the film thickness was 530Å for Ag and 490Å for Au to achieve optimum coupling).

4. MEASUREMENTS

i) Physisorbed H_2 on Au

Fig.2 shows part of an adsorption isotherm of molecular hydrogen on gold at 9.93 K, measured with SP. The equilibrium film thickness and the SP width $\Theta_{1/2}$ are plotted versus the pressure in the experimental cell. Distinct steps in thickness at monolayer completion can be seen (the buildup of the first two layers is not resolved). The rounding of the monolayer steps (when comparing to the sharp steps observed in ellipsometric measurements on crystalline graphite⁸) is due to imperfections on the thermally evaporated gold film. One Ångström of molecular hydrogen corresponds to a shift of $3.3 \cdot 10^{-3}$ deg in Θ_{res} on gold ($\epsilon_{H_2} = 1.295$). Even for these ultrathin films changes in the halfwidth of the resonance can be seen accompanying the successive buildup of the monolayers.

We also used the technique to measure the wetting behavior of H_2 on gold. Molecular hydrogen is expected to show triple-point wetting, i.e. below the triple-point temperature T_t it exhibits only a limited

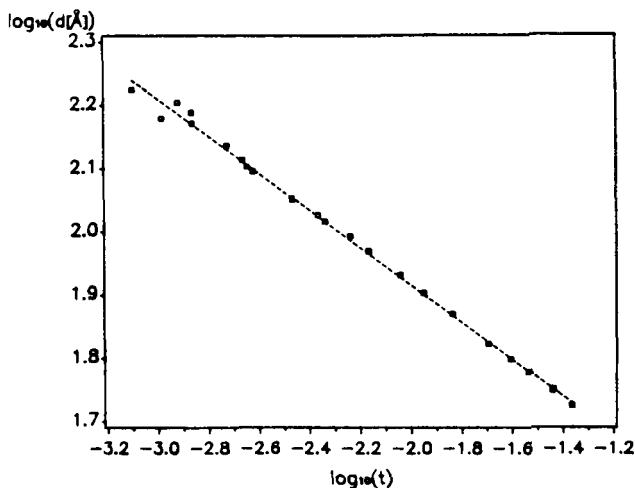


Figure 3: Triple-point wetting of H_2 on Au: critical behavior of the maximum film thickness d_{max} at s.v.p. vs. the reduced temperature $t = |(T - T_t)/T_t|$ (T_t : triple-point temperature), giving a slope of $-1/3.40$.

film thickness d_{max} at s.v.p. d_{max} rises with T and diverges at T_t . Fig.3 shows a double-log plot of d_{max} versus the reduced temperature $t = |(T - T_t)/T_t|$, showing the critical behavior which can be described by a power law $d_{max} \sim t^{-1/n}$. We find $n = 3.40$ in good agreement with a value published by Migone et al. for hydrogen adsorption on silver⁹.

ii) Quench-condensed H_2 on Ag

Figure 4 shows results obtained during annealing of a molecular hydrogen film prepared by quench-condensation at 1.3K onto the prism base. The temperature was raised stepwise in the course of the experiment. The film thickness stays constant up to a temperature of 2.3K (the slight thickness increase at the beginning results from the condensation of residual H_2 molecules emanating from the feeding capillary). Upon raising the temperature further, the film starts to evaporate. After some time the evaporation stops and the film remains at constant thickness (about half its initial value in this case) even if the temperature is raised further. At around 3K evaporation sets in again until the film is virtually gone (apart from a few more tightly bound monolayers). Following the course of the SP halfwidth $\Theta_{1/2}$ we observe a drastic broadening of the resonance during the first thinning of the film towards the plateau thickness, until at complete evaporation it relaxes back to its initial value. Apparently the quench-condensed hydrogen film changes its nature distinctly in a narrow temperature region from a more loosely to a tightly bound system (with roughly the bulk value for the binding energy) showing a strongly enhanced SP scattering, i.e. with inhomogeneities on the order of the light wavelength (details of these results will be published elsewhere¹⁰).

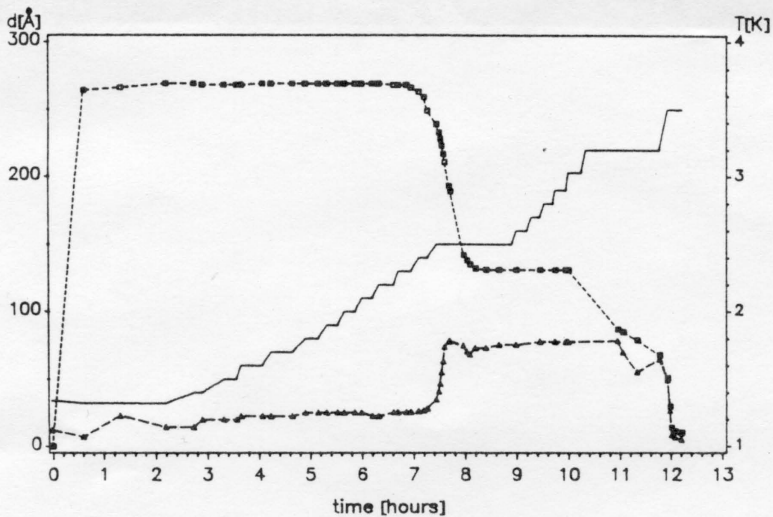


Figure 4: Thermal annealing of quench-condensed H₂: temperature (straight line), film thickness (squares) and SP width (triangles, arbitrary units, higher values indicating enhanced scattering) during the course of the experiment.

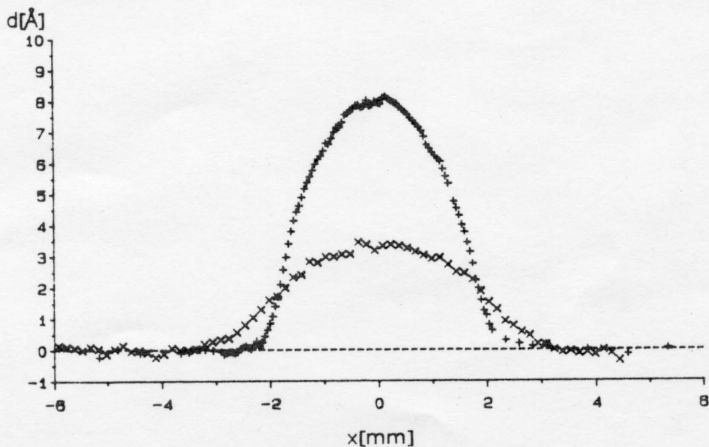


Figure 5: Spreading of PDMS on Ag: thickness profiles of a 6 μ l volume droplet 50 minutes (+) and 6 hours (x) after deposition.

iii) Spreading of molecularly thin oil films

Scanning the incident light beam across the prism base provides additional lateral resolution for the measurements with SP. We used this to measure thickness profiles of tiny polydimethylsiloxane (PDMS) drops deposited on silver substrates and their evolution in time. The lateral resolution is determined by the size of the illuminated spot on the prism, in our case about $100\mu\text{m}$. Fig.5 shows a drop of 6pl volume 50 minutes and 6 hours after deposition. Even with scanning subångström resolution is achieved. The noise on the data is mainly due a small longtime drift of the optical setup leading to errors in the background correction. A droplike shape is still observed even though the maximum thickness of the drop is only around one monolayer (the PDMS molecules lie flat on the surface and have a thickness of about 7Å ¹¹.) The shape of the drops can be fitted well by a spherical cap (with a very small smeared out foot), whereas a Gaussian gives much worse agreement¹².

5.SUMMARY

SP resonance measurements are a very sensitive probe for the thickness of thin films. The sensitivity is similar to ellipsometry; since only intensities are measured strain in the windows of the experimental cell is not a problem. Additional information in structural changes within the film is obtained by observing the SP resonance width. We present measurements of an adsorption isotherm of molecular hydrogen, the annealing behaviour of quench- condensed hydrogen and the time evolution of profiles of small oil drops.

6.ACKNOWLEDGEMENTS

This work was supported by the Sonderforschungsbereich 306 of the Deutsche Forschungsgemeinschaft.

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