Ad- and desorption of Rb atoms on a gold nanofilm measured by surface plasmon polaritons

C Stehle, H Bender, F Jessen, C Zimmermann and S Slama
Physikalisches Institut, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 14, D-72076 Tübingen, Germany
E-mail: slama@pit.physik.uni-tuebingen.de

New Journal of Physics 12 (2010) 083066 (9pp)
Received 15 June 2010
Published 31 August 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/8/083066

Abstract. Hybrid quantum systems made of cold atoms near nanostructured surfaces are expected to open up new opportunities for the construction of quantum sensors and for quantum information. For the design of such tailored quantum systems, the interaction of alkali atoms with dielectric and metallic surfaces is crucial and has to be understood in detail. Here, we present real-time measurements of the adsorption and desorption of rubidium atoms on gold nanofilms. Surface plasmon polaritons (SPP) are excited at the gold surface and detected in a phase-sensitive way. From the temporal change of the SPP phase, the rubidium coverage of the gold film is deduced with a sensitivity better than 0.3% of a monolayer. By comparing the experimental data with a Langmuir-type adsorption model, we obtain the thermal desorption constant and the sticking probability. In addition, laser-induced desorption is also observed and quantified.

Contents
1. Introduction 2
2. Experimental setup 3
3. Theoretical model 3
4. Observations 5
5. Conclusion 8
Acknowledgments 9
References 9

1 Author to whom any correspondence should be addressed.
1. Introduction

Surface plasmon polaritons (SPP) have been used for a long time as sensitive detectors, e.g. for biomolecules. These highly sensitive detectors are simple to build and in this sense complementary to other, more specialized, methods applied in surface physics, such as Auger electron spectroscopy, photoemission spectroscopy or electron diffraction techniques. SPP are mainly excited in the so-called Kretschmann configuration by internal reflection of a laser beam from a surface that is coated with a thin metal film [1]. Such methods are necessary because surface plasmons cannot be excited directly. This is due to the plasmonic dispersion relation, which is incompatible with the light cone in vacuum. However, it can be matched with the evanescent light field of an internally reflected laser beam by tuning the incidence angle. This gives rise to a resonant effect at the so-called plasmon angle $\alpha_{\text{pl}}$. Particles that are close to or stick to the metal film shift the surface plasmon angle. This can be understood in a simple picture: the additional atoms form a layer above the gold surface with a certain refractive index. The dispersion relation of the SPP depends on this refractive index and is slightly modified. This shifts also the angle under which the dispersion relation is matched. In principle, such shifts can be detected very sensitively by measuring the phase of the reflected light beam which changes dramatically at the plasmon angle. However, the fact that the reflectivity is zero at the plasmon angle, i.e. the power of the laser beam is completely transferred into a plasmonic excitation, broadens the detectable phase shift and limits the sensitivity [2]. Recently, a new excitation scheme has been introduced that avoids this problem. In this method the phase of the incident laser field is electronically controlled by a feedback loop [3]. In the work presented here, this scheme is used for the first time to actually measure the optical properties of a sample. The work is mainly motivated by recent progress in the field of surface quantum optics, atom chips and hybrid quantum systems. Such tailored quantum systems made of cold atoms near nanostructured surfaces are expected to open up new opportunities for the construction of quantum sensors and for quantum information. In this context, we recently studied clouds of ultracold atoms coupled to evanescent waves near solid surfaces [4]. The enhancement of such optical near-fields by the excitation of surface plasmons has been known for some time [5], but only recently have proposals been put forward to generate plasmonic nanopotentials for the manipulation and trapping of cold atoms [6, 7]. For the design of such traps, surface potentials such as the Casimir–Polder potentials [8] have to be taken into account, and some effort has been invested by the cold atoms community into studying dissipative forces [9]–[13]. However, additional potentials from particles adsorbed at the surface have been given little consideration. As has been shown experimentally [14], such potentials can dramatically influence atom traps near surfaces. Thus, it is crucial to understand and control atomic adsorption, e.g. by laser-induced atomic desorption (LIAD) [15, 16]. LIAD is used in the cold atoms community mainly for quickly raising the vapor pressure in a vacuum cell for a rapid loading of magneto-optic traps. It has been demonstrated for a variety of atomic species (Rb, Cs, Na, Na$_2$, Ni, Zn, Sn and K) and substrates (pyrex, porous silica, sapphire, glass and stainless steel), most of which were coated with silane or paraffin [17]. However, desorption of Rb from a gold surface has not been investigated until now. Furthermore, fascinating ideas have been proposed that rely on the controlled adsorption of atoms on semiconductor surfaces, which might prove to be an important technological step toward the manipulation of electronic nano devices [18].

Here, we report on adsorption of thermal rubidium atoms on a gold nanofilm. The rubidium coverage is monitored by the phase shift in the excitation spectrum of SPP. By rapidly changing
the rubidium vapor pressure, the balance between adsorption and thermally induced desorption is perturbed and re-equilibration of the adsorbate coverage is monitored in real time. The observations are compared to a simple Langmuir-type model and the parameters of the model are extracted from the data.

2. Experimental setup

The ad- and desorption of rubidium atoms are observed by phase-sensitive detection of the surface plasmon resonance. The experimental setup is shown in figure 1. The beam from a grating stabilized diode laser (laser 1, wavelength near the D2 line of $^{87}$Rb of $\lambda = 780$ nm, laser power $P = 10$ mW and laser bandwidth 2 MHz) is internally reflected from the gold-coated surface of a dielectric prism. The incident angle $\alpha$ at which the laser hits the prism surface can be adjusted with a mirror mounted on a mechanically driven translation stage (TS). It shifts the beam relative to a lens that guides the beam to the prism surface. The position of the TS is monitored with an auxiliary laser beam and a position-sensitive diode (PSD). The guiding lens is the second lens in a 2f telescope, with the first lens being attached to the TS. Thus, the incident beam is collimated at the prism surface. At a characteristic plasmon angle $\alpha = \alpha_{pl}$ surface plasmons are excited by the p-polarized fraction of the incoming light. The incident light is absorbed by the plasmon excitation and the reflectivity for p-polarized light $r_p$ drops to a minimum. If the impedance matching is fulfilled, i.e. the gold layer has the right thickness, reflection can be completely suppressed, as shown in the theoretical curve in figure 2. Experimentally, the reflected light intensity at the minimum was 4.3%. If rubidium atoms are adsorbed, the value of the plasmon angle shifts and the phase of the p-polarized fraction of the reflected light field $\phi_p$ changes. The phase change is monitored with a standard HC setup [19]. This allows us to measure the ellipticity of the reflected light field: it transforms the circular components into orthogonal linearly polarized waves by a $\lambda/4$ plate and separates these with a beamsplitter. Both waves are separately detected on photodiodes and subtracted from each other. The acquired signal depends on the handedness and the magnitude of the ellipticity and is proportional to $r_p \sin(\phi_p)$. A PI (Servo Electronics) feeds this signal to an EOM that controls the phase of the incident laser light [3]. This locks the HC signal to zero such that the control voltage at the EOM is directly proportional to $\phi_p$.

The gold film on the prism surface has been fabricated by e-beam evaporation and has a thickness of approximately 50 nm. Below the gold film, a very thin layer of titanium has been added to improve the adhesion of the gold to the glass substrate. The prism is placed inside a vacuum chamber at a base pressure of $5 \times 10^{-9}$ mbar and is mounted on a temperature-controlled heating unit. The partial pressure of Rb in the chamber is controlled by a resistively heated dispenser and can be raised within a few minutes to several $10^{-6}$ mbar. Laser-induced desorption of Rb atoms can be investigated with an additional blue laser beam at a wavelength near 406 nm and a maximum power of 20 mW (laser 2).

3. Theoretical model

The interpretation of our experiment is based on the observation that, according to Brunauer, Emmet and Teller (BET), only fractions of a monolayer can be adsorbed if the vapor pressure of an adsorbant is smaller than the saturation vapor pressure $p < p_{sat}$ [20]. Thus, the surface
Figure 1. Experimental setup. Laser 1 excites plasmons at the surface of a gold-coated prism inside a vacuum chamber with a variable rubidium (Rb) vapor pressure. The angle $\alpha$ at which the laser beam hits the surface is varied with a TS. It shifts the beam relative to the lens that guides the beam to the prism surface. The position of the TS is monitored with an auxiliary laser beam and a PSD. The beam reflected from the surface is analyzed by a Hänsch–Couillaud (HC) setup. It consists of a $\lambda/4$ retardation plate, a polarizing beam splitter cube (PBC) and a pair of differential photodiodes. The recorded signal is controlled by a PI feedback loop, which acts on the phase of the incident light field via an electro-optic modulator (EOM). The feedback voltage is directly proportional to the phase of the reflected light field $\phi_p$. For laser-assisted desorption of atoms the gold surface can be exposed to a second laser beam (laser 2).

Coverage $\Theta$ only takes values between 0 and 1, i.e. $0 < \Theta < 1$. We model the temporal change of the surface coverage by the rate equation

$$\dot{\Theta} = -C \Theta + I_{in} \sigma S(\Theta),$$

with a desorption constant $C$, an impinging flux of atoms on the surface $I_{in}$, a typical area per adsorbed atom of $\sigma = 10^{-13} \text{cm}^2$ and a sticking probability $S(\Theta)$. The atomic flux hitting the surface is given by $I_{in} = n v / 4$, with the factor 4 following from integrating the Knudsen cosine law over a half-sphere, the ideal gas vapor density $n = p / k_B T$ and the thermal velocity of the atoms $v = (2k_B T / m)^{1/2}$. The temperature $T$ here is that of the surrounding vacuum.
chamber. For simplicity, we define the flux per pressure $R$ in units of adsorbed monolayers via $I_{\text{ads}} \equiv Rp$, i.e. $R = \sigma \left(1/8mk_{B}T\right)^{1/2}$. The sticking probability is taken from the Langmuir model $S(\Theta) = S_{0} \cdot (1 - \Theta)$, with the initial sticking probability $S_{0}$ [21]. Note that $S(\Theta)$ vanishes for full coverage ($\Theta = 1$). This guarantees that only fractions of a monolayer can be adsorbed. With these definitions, (1) reads

$$\dot{\Theta} = -(C + S_{0}Rp)\Theta + S_{0}Rp.$$  

(2)

In equilibrium ($\dot{\Theta} = 0$), the surface coverage is given by

$$\Theta_{\text{eq}} = \frac{1}{1 + C/S_{0}Rp}.$$  

(3)

We would like to point out that throughout the paper, ‘equilibrium’ always means equilibrium of the adsorbate coverage on the surface with the gas vapor. The equilibrium coverage depends on the pressure in the chamber. If the pressure is rapidly changed, a new equilibrium is exponentially reached within a $1/e$ time scale:

$$\tau = \frac{1}{C + S_{0}Rp}.$$  

(4)

as can be deduced from (2).

4. Observations

We measure the adsorption of rubidium with the above-mentioned setup by two different methods. In the first method the incidence angle is scanned, and from the signal obtained the position of the plasmon angle is determined. This method is applicable for a plasmon angle that changes only a little during the scan time of approximately 1 min. Figure 3 shows an example. The relation between the shift of the plasmon angle $d\alpha_{\text{pl}}$ and the thickness of the adsorbed layer...
Figure 3. Phase $\phi_p$ versus incidence angle shift $d\alpha$ before (i) and after (ii) adsorption of Rb atoms.

dl is taken from a four-layer matrix model (layer 1: glass substrate; layer 2: gold film; layer 3: Rb adsorbate; layer 4: vacuum), which takes multiple reflections at the boundaries into account [22]. With the dielectric constant of gold $\epsilon_{\text{Au}} = -22.9 + 1.42 \times i$ and Rb $\epsilon_{\text{Rb}} = -4 + 0.42 \times i$ [23, 24], the result is $d\alpha_{pl}/dl = 0.1^\circ \text{ nm}^{-1}$. Note that for all values of surface coverage reported in this paper the mean distance between adsorbed atoms is much smaller than the wavelength. The rubidium layer can for that reason be described by its refractive index even when the surface coverage is smaller than one monolayer. The observed shift of the plasmon angle in figure 3 of $d\alpha_{pl} = 0.072^\circ$ thus corresponds to an adsorbed Rb layer thickness of $l = 0.72$ nm.

The second method records the phase $\phi_p$ with the incidence angle fixed at the plasmon angle. Adsorption and desorption of atoms can now be observed in real time by looking at the temporal change of the phase $\phi_p$. For not too large variations of $\alpha_{pl}$ the relation between plasmon angle and phase is linear with a slope of $d\phi_p/d\alpha_{pl} = 42.1$ rad deg$^{-1}$ that is taken from the left curve in figure 3. After adsorption of Rb (right curve) the slope is by $d\phi_p/d\alpha_{pl} = 35.1$ rad deg$^{-1}$ slightly smaller. For large changes of the plasmon angle the working point is shifted from the linear regime to a regime where the phase change saturates. Thus, the second method can only be applied for small changes of the plasmon angle unless the incidence angle is recalibrated. Typical data are shown in figure 4. In figure 4(a) the Rb vapor pressure is quickly increased by activating the dispenser for about 80 s (curve (ii)). The pressure is determined with a standard ion gauge. Curve (i) shows the resulting change of the phase $\Phi_p$. During the pulsed increase of vapor pressure, the rubidium coverage also grows and remains at an increased value after the pulse. Figure 4(b) shows a similar measurement with higher resolution, which allows us to estimate the sensitivity of the method. After low-pass filtering of the signal with an integration time of $T = 50$ ms, the noise of the phase signal is of the order of $\Delta \phi_p = 5 \times 10^{-3}$ rad. At this noise level, the uncertainty of the measured layer thickness is $\Delta l = \Delta \phi_p \cdot d\alpha_{pl}/d\phi_p \cdot dl/d\alpha_{pl} = 1.2$ pm. With an average distance between two atoms given by twice the covalent radius of Rb of $2r_c = 440$ pm, the sensitivity amounts to better than $\Delta l/2r_c = 0.3\%$ of an adsorbed monolayer. This sensitivity corresponds to a resolvable relative refractive index change of $\Delta n/n = 2 \times 10^{-6}$.

In the experiment, the gold surface is heated to a temperature of $T_s = 68^\circ \text{C}$. The resulting Rb saturation vapor pressure of $p_{\text{sat}} = 2 \times 10^{-5}$ mbar is one order of magnitude larger than the maximum Rb vapor pressure in the experiment of $p_{\text{max}} = 2 \times 10^{-6}$ mbar. The above assumption of a fractional coverage is thus well justified. In figure 5 the observed coverage $\Theta$ is plotted during and after a temporal increase of the Rb vapor pressure. The initial growth rate at $\Theta \approx 0$
Figure 4. (a) Observed phase shift (i) and Rb vapor pressure (ii) after activating the Rb dispenser at time $t = 0$ for a period of 80 s. (b) Estimation of the experimental phase noise level.

Figure 5. Observed monolayer coverage (blue solid dots, right vertical axis) during and after a temporal increase of the Rb vapor pressure (red open circles, left vertical axis). The linear coverage growth during the first 20 min is fitted by the dashed line through the origin. The line is extrapolated to unity coverage (horizontal dashed line) and the intersection is projected onto the time axis (vertical dashed line). The decay of the coverage after the pulse is fitted with an exponential function. This is done for times larger than 200 min such that the pressure in the chamber has almost saturated.

is derived by linearly fitting the increase at small values of coverage of $\Theta < 0.2$. This is the case for the first 20 min. Here, the pressure is linearly increasing across a value of $p = 1 \times 10^{-7}$ mbar. The slope of the fitted line (dashed line through the origin) is $d\Theta/dt = (150 \text{ min})^{-1}$. For guiding the eye we extrapolate the fit to unity coverage (dashed horizontal line) and project the intersection with it onto the time axis (vertical dashed line). Putting the acquired initial
Figure 6. Laser-induced desorption of Rb. If the surface is exposed to blue laser light, the surface coverage starts to decrease.

growth rate into (2), setting $\Theta = 0$ and $p = 1 \times 10^{-7}$ mbar, the initial sticking coefficient can be determined to be $S_0 = 0.8\%$. After about 100 min we switch off the rubidium dispenser and the vapor pressure starts to decrease exponentially. Now the atoms thermally desorb and also the coverage decays exponentially. The thermal desorption constant $C = C_{th}$ can be determined from (4) by measuring the $1/e$ decay time $\tau$. Fitting an exponential curve to the data yields $\tau = 4.7 \times 10^3$ s. For this fit, only those data points at times larger than 200 min are used, where the vapor pressure has almost saturated at a value of $p = 7 \times 10^{-8}$ mbar. For the desorption constant we obtain $C = (1/\tau) - S_0 R p = 1.3 \times 10^{-4}$ s$^{-1}$. In order to show the consistency of the model with the determined parameters the equilibrium coverage is calculated from (3) to be $\Theta_{eq} = 0.4$. This value is comparable to the observed value in figure 5 of $\Theta_{eq} = 0.5$.

The equilibrium coverage can be further reduced by exposing the surface to a laser beam with a wavelength near 406 nm ($\approx 20$ mW laser power and beam diameter 1 mm). Figure 6 shows the resulting change of the surface coverage $d\Theta$. As soon as the blue laser is turned on, the coverage decreases in time. The behavior during the first 50 s is a subject worthy of further studies, which are beyond the scope of this paper. The latter behavior shows a linear decrease with a rate of $\dot{\Theta} = -4.4 \times 10^{-5}$ s$^{-1}$. The total desorption coefficient is now the sum of the thermal and the laser-induced desorption coefficient $C = C_{th} + C_{li}$. With (2) and for $\Theta = 0.5$ and a pressure of $p = 2 \times 10^{-7}$ mbar, the total desorption coefficient amounts to $C = 3.1 \times 10^{-4}$ s$^{-1}$. This results in a pure laser-induced desorption rate of $C_{li} = 1.8 \times 10^{-4}$ s$^{-1}$ at a laser power of approximately 20 mW. The new equilibrium coverage of $\Theta_{eq} = 0.42$ is reached within a $1/e$ time of $\tau = 1.9 \times 10^3$ s.

5. Conclusion

We have applied a recently introduced method [3] for detecting de- and adsorption phenomena by means of phase-sensitive detection of a surface plasmon resonance to rubidium on a gold surface. Adsorption and desorption of Rb were observed and interpreted with a rate model.
We reach a sensitivity better than 0.3% of a monolayer, i.e. a refractive index unit change of $\Delta n = 2 \times 10^{-6}$ RIU within an integration time of 50 ms. This is comparable to typical sensitivities reached with surface plasmon resonance sensors [25]. The observed sensitivity in this paper is limited by technical noise, which leaves much room for substantial improvement, e.g. by a shot-noise-limited detection scheme, by suppression of laser frequency noise and by longer integration time. As has been shown in [3], a resolution of $\Delta n = 2 \times 10^{-8}$ RIU within an integration time of 0.1 s seems feasible even far above the shot-noise limit. Such a sensitivity exceeds the best values reported for conventional detectors, e.g. in [26]. By comparing the experimental data with a Langmuir-type adsorption model, we found a desorption constant of $C = 1.3 \times 10^{-4}$ s$^{-1}$ and an initial sticking probability of $S_0 = 0.8\%$. Laser-assisted desorption has been observed. A desorption coefficient of $C_{li} = 1.8 \times 10^{-4}$ s$^{-1}$ was determined for a laser power of approximately 20 mW.

Acknowledgments

We acknowledge financial support from the DFG within the EuroQuasar program of the ESF and we thank A Hemmerich for inspiring discussions.

References

[1] Kretschmann E and Raether H 1968 Z. Naturforsch. A 28 2135
[2] Ran B and Lipson S G 2006 Opt. Express 14 5641
[3] König T, Weidemüller M and Hemmerich A 2008 Appl. Phys. B 93 545
[4] Bender H, Courteille P, Zimmermann C and Slama S 2009 Appl. Phys. B 96 275
[5] Esslinger T, Weidemüller M, Hemmerich A and Hänsch T W 1993 Opt. Lett. 18 450
[6] Chang D E, Thompson J D, Park H, Vuletic V, Zibrov A S, Zoller P and Lukin M D 2009 Phys. Rev. Lett. 103 123004
[7] Murphy B and Hau L V 2009 Phys. Rev. Lett. 102 033003
[8] Casimir H B G and Polder D 1948 Phys. Rev. 73 360
[9] Sandoghdar V, Sukenik C I, Hinds E A and Haroche S 1992 Phys. Rev. Lett. 68 3432
[10] Sukenik C I, Boshier M G, Cho D, Sandoghdar V and Hinds E A 1993 Phys. Rev. Lett. 70 560
[11] Grisenti R E, Schöllkopf W, Toenness J P, Hegerfeldt G C and Köhler T 1999 Phys. Rev. Lett. 83 1755
[12] Obrecht J M, Wild R J, Antezza M, Pitaevskii L P, Stringari S and Cornell E A 2007 Phys. Rev. Lett. 98 063201
[13] Bender H, Courteille Ph W, Marzok C, Zimmermann C and Slama S 2010 Phys. Rev. Lett. 104 083201
[14] McGuirk J M, Harber D M, Obrecht J M and Cornell E A 2004 Phys. Rev. A 69 062905
[15] Gozzini A, Mango F, Xu J H, Alzetta G, Maccarrone F and Bernheim R A 1993 Nuovo Cimento D 15 709
[16] Meucci M, Mariotti E, Bicchi P, Marinelli C and Mio L 1994 Europhys. Lett. 25 639
[17] Klempt C, van Zoest T, Henninger T, Topic O, Rasel E, Ertmer W and Artl J 2006 Phys. Rev. A 73 013410
[18] Judd T E, Scott R G, Sinuco G, Montgomery T W A, Martin A M, Krüger P and Fromhold T M 2010 New J. Phys. 12 063033
[19] Hänsch T W and Couillaud B 1980 Opt. Commun. 35 441
[20] Brunauer S, Emmett P H and Teller E 1938 J. Am. Chem. Soc. 60 309
[21] Masel R I 1996 Principles of Adsorption and Reaction on Solid Surfaces (New York: Wiley)
[22] Deutsch I H, Spreew R J C, Rolston S L and Phillips W D 1995 Phys. Rev. A 52 1394
[23] Etchegeoin P G, Le Ru E C and Meyer M 2006 J. Chem. Phys. 125 164705
[24] Smith N V 1970 Phys. Rev. B 2 2840
[25] Homola J, Yee S S and Gauglitz G 1999 Sensors Actuators B 54 3
[26] Kabashin A V, Patkovskys S and Grigorenko A N 2009 Opt. Express 17 21191

New Journal of Physics 12 (2010) 083066 (http://www.njp.org/)