Laser-induced atomic adsorption: A mechanism for nanofilm formation

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received 29 July 2013; accepted in final form 31 October 2013
published online 29 November 2013

PACS 34.35.+a – Interactions of atoms and molecules with surfaces
PACS 32.80.Fb – Photoionization of atoms and ions
PACS 73.30.+y – Surface double layers, Schottky barriers, and work functions

Abstract – We demonstrate and interpret a technique of laser-induced formation of thin metallic films using alkali atoms on the window of a dense-vapour cell. We show that this intriguing photo-stimulated process originates from the adsorption of Cs atoms via the neutralization of Cs$^+$ ions by substrate electrons. The Cs$^+$ ions are produced via two-photon absorption by excited Cs atoms very close to the surface, which enables the transfer of the laser spatial intensity profile to the film thickness. An initial decrease of the surface work function is required to guarantee Cs$^+$ neutralization and results in a threshold in the vapour density. This understanding of the film growth mechanism may facilitate the development of new techniques of laser-controlled lithography, starting from thermal vapours.

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Atomic vapours in optical cells are convenient and ubiquitous systems in many studies of matter-radiation interaction. Interactions of the atomic samples with the cell walls are often unavoidable and may interfere with the processes studied, because of the production of stray electric fields [1], spin depolarization [2], surface conductivity [3] and optical transparency impairment due to the reactivity of hot alkali atoms with the glass. On the other hand, these atom-surface interactions can be explored for applications in fundamental as well as in applied physics. For example, alkali adsorbates represent a controllable source of atoms via light-induced desorption [4]. Selective, laser-controlled quantum adsorption of cold atoms for realization of 2D atomic waveguides remains a theoretical possibility [5–7], to be experimentally demonstrated. The perspective of controlling adsorption using light opens the way to grow nanostructures directly on a dielectric surface, which is particularly attractive for such applications as building circuitry with the aim of manipulating cold and ultracold atomic samples close to surfaces [8]. We demonstrate here the laser-induced adsorption of caesium atoms from a dense hot vapour, leading to the formation of a thin caesium film on a dielectric window when illuminated with a laser resonant with the Cs D$_2$ transition. The occurrence of this photo-stimulated atom-surface process has essentially gone unnoticed or ignored, in spite of its potential relevancy in studies involving alkali vapour cells [9] or as a new lithographic technique [10], for which the fundamental mechanisms have been elusive until now [11].

The basic experimental configuration shown in fig. 1(a) consists in a low-power (a few mW/mm$^2$, beam radius...
≈ 1 mm) cw laser beam sent through an optical cell containing a hot vapour of caesium atoms. The laser frequency is tuned close to the frequency of the alkali D2 transition (λ = 852 nm). Surprisingly, we observe the formation of a metallic film on the illuminated spot at the interface between the window of the cell and the vapour [11]. The thickness profile of the film follows the transverse intensity of the pump laser beam (figs. 1(b) and (c)), which suggests potential applications in the initial few-layers regime, as a function of the atomic vapour density: (a) in a sapphire window, for $I = 3.2 \text{ mW/mm}^2$ and $T_w = 215 \text{ °C}$; (b) in a quartz window. Open circles: $T_w = 215 \text{ °C}$; solid circles: $T_w = 190 \text{ °C}$. Solid lines: fits obtained from eqs. (1)–(5).

The metallic film induced by laser is characterized by two distinct growth rates (see fig. 1[d]). The typical growth rate change observed at $t \approx 15 \text{ min}$ occurs when the average film thickness is on the order of a few atomic layers. We study the film formation in the initial regime: Figures 2(a) and (b) show the behaviour of the film growth rate as a function of the atomic density in the vapour for two different dielectric substrates (sapphire and quartz, respectively) and for different sets of window temperature, laser frequency detuning and power. We finely control the temperature of the cell windows and of the reservoir. The latter determines the vapour density and is set at a few tens of °C colder than the cell body. The temperature of the reservoir ranges between 150 °C and 190 °C, corresponding to atomic densities between $2 \times 10^{14}$ and $1.2 \times 10^{15} \text{ cm}^{-3}$. The measurements have been made at two different temperatures of the window, 190 °C and 215 °C. The temperatures are stabilized with a precision of 1 °C, leading to a relative uncertainty of ≈ 4% in the atomic density. The uncertainty on the growth rate is ≈ 15%.

The growth rate is linear with atomic density, suggesting a one-atom process. However, there is a peculiar density threshold for film formation. All other parameters being equal, this threshold is larger for quartz (fig. 2(b)) than for sapphire (fig. 2(a)) surfaces, increases with the temperature of the window (fig. 2(b)) and does not depend on pump power or frequency (figs. 2(a) and (b)), which only affect the efficiency of the film growth.

The growth rate increases cubically with the pump laser intensity (fig. 3(a)) for a frequency detuned from resonance so as not to saturate the atomic transition (detunings on the order of the transition Doppler linewidth). Thus, a three-photon process is the basis of the film growth on the surface. Notice that three 852 nm photons have a total energy of approximately 4.37 eV, sufficient to ionize a caesium atom (ionization energy ≈ 3.89 eV). This cubic dependence has been verified for various detunings on both sides of the atomic one-photon resonance, in the non-saturating regime (fig. 3(a)). Complementarily, using two lasers of similar frequencies, intensities $I_1$ and $I_2$ and with...
no fixed phase relationship, we studied the role of laser coherence effects on the film formation. Because the lasers frequency is close to resonance with the Cs D₂ transition, it is expected that, in a first step, the excited level 6P₃/₂ will be significantly populated by any of the lasers, with a probability proportional to the total intensity. Indeed, series of experiments on the film formation using different combinations of the intensities I₁ and I₂ pointed to the interpretation that the growth rates are only compatible with the dependence expected for coherent two-photon absorption by 6P₃/₂ excited atoms, in both the resonant and the non-resonant regimes (see figs. 3(a) and (c)). This interpretation is further supported by the observation that the growth rate (see fig. 3(b)) follows the 6P₃/₂ fluorescence spectrum, which exhibits a typical minimum at resonance, due to excitation quenching at the surface [14]. Moreover, for small detunings, the laser saturates the D₂ transition and the two-photon absorption from the saturated 6P₃/₂ excited state results in a growth rate increasing quadratically with the beam intensity (fig. 3(a)).

Therefore, our measurements show that, in the early stages of film formation, there is a linear growth with vapour density and a cubic dependence on the laser intensity. These are our main results, which demonstrate that, among many multiple-atom and multiphoton processes near the surface, the film genesis is due to single-atom ionization with three photons. This is a low-probability mechanism, which explains the relatively slow process of alkali film formation on windows of vapour cells in the presence of low-power resonant lasers. The atomic-density threshold further limits the conditions in which such a laser-induced atom-surface process can be observed. Therefore, this process is not ordinarily observed in low-density experiments.

To explain these observations, the processes that occur at the interface are described using simplified rate equations, in terms of adsorption and desorption rates. The interaction between atoms and surfaces originates either from the dipolar van der Waals interaction (physisorption, see for instance [15,16]) or from charge exchange with the substrate (chemisorption, see for instance [17]). Pure physisorption and chemisorption constitute limiting cases and varying degrees of hybridization can actually be present. Adsorption of neutral atoms from the thermal vapour acknowledgedly falls into the physisorption category, while the light-induced film, intermediated by ions, involves stronger charge exchange processes and falls into the chemisorption one. These two processes, as expected, evolve at very different rates: at the typical temperatures we worked, we measured the desorption rate of the thermal atoms to be on the order of 10^3 s⁻¹, while the desorption rate of the film (neutralized ions) is on the order of 10⁻⁵ s⁻¹ (see footnote ²).

The evidence for very different time scales for the two processes in our system allows us to separately consider the contributions from the neutral atoms in the vapour and from the neutralized ions. Therefore, for the very initial regime of film formation, the two equations can take the same general form:

$$\frac{dN_j}{dt} = p_j \sqrt{\frac{k_B T_w}{2 \pi m}} n_j \sqrt{\frac{1}{\tau_j}} e^{-E_j/k_B T_w} N_j,$$  

(1)

where the subscript index j = A, I stands for the thermal neutral atoms (A) and the neutralized ions (I). N_j is the surface density of the j-kind adsorbed atoms (adatoms) in the area illuminated by the laser, p_j is a sticking coefficient, n_A (n_I) is the atomic (ionic) density in the vapour, k_B is the Boltzmann constant, m is the atom mass and T_w is the window temperature. The first and second terms in eq. (1) are the adsorption and an Arrhenius-like [18] desorption rate per unit area, respectively. The residence time of the j-adatoms in the surface potential well is characterized by the adsorption energy E_j and by the time constant τ_j, associated to physisorption (j = A) and chemisorption (j = I) bound states. The adatom surface density in eq. (1) is proportional to the measured average film thickness L, through a coefficient N_{ml}/(2πr), where r is the caesium atom radius (r = 0.26 nm) and N_{ml} the caesium surface density for a monolayer (N_{ml} = 4.7 × 10^{14} at/cm²).

Before the light is turned on, the physisorbed atoms are in thermal equilibrium with the surface, forming a sub-monolayer film, i.e., the fluxes of thermal particles going to and from the surface are taken as being the same. Although they do not directly participate in the film growth, their equilibrium density on the surface determines the effective substrate for the light-induced ions incident from the vapour. Let us therefore first analyse the thermal rate equation (eq. (1)) for NA₀(t). The equilibrium density of adatoms N_A₀ on the surface results from the balance between the desorbed and adsorbed neutral atomic fluxes on the surface and is obtained by solving the thermal rate equation (1) for dN_A/dt = 0:

$$N_{A₀}(T_w, n_A) = p_A \sqrt{\frac{k_B T_w}{2 \pi m}} T_A e^{E_A/k_B T_w} n_A.$$  

(2)

It is responsible for the density threshold observed in figs. 2(a) and (b). Alkali adatoms are known to significantly lower the work function of metal substrates and are used to increase surface ion or electron emission [19]. Studies of the interaction of alkali atoms with insulators are less numerous but confirm that alkali adatoms also lower the work functions of dielectric substrates [20].

The interaction between atoms or ions and a partially caesiated solid surface depends on the relative electronegativities of the surface and the impinging species [21]. The coefficient p_A equal to unity. The light-induced film desorption rates are obtained by measuring the decrease of the film thickness when the laser is turned off, all other conditions being the same.
relative electronegativity, in turn, depends on the pre-existing adatom coverage \( \theta \) (see fig. 4). Coverage is defined as the ratio between the density of adatoms and the density \( N_{\text{at}} \) for a monolayer. At low Cs coverage (fig. 4(a)), the surface is more electronegative than the Cs atoms, and hence, the impinging Cs atoms transfer their valence electron to the substrate [20]. The positive core of adatoms then gives rise to an “electrical double layer” on the surface [22]. A higher coverage of Cs adatoms lowers the work function of the solid substrate [23] and thus diminishes the relative electronegativity between the adatoms and the surface (fig. 4(b)).

As a result of the thermal surface caesiumisation, two interaction regimes may therefore occur between the caesiated surface and impinging Cs\(^+\) ions. If the Cs coverage is low, the ions are repelled from the surface by the adsorbed atoms, and their outward positive pole prevents the ion from forming. If the Cs coverage is sufficiently high to lower the substrate work function to less than the atom ionization energy, an electron can be transferred from the substrate to the ion, thus neutralizing it [24]. The vapour density threshold, which varies with the window temperature, therefore corresponds to a thermal coverage threshold. Of course, this threshold also depends on the window material, as shown in figs. 2(a) and (b). For a given material, the variation of the threshold coverage with temperature is given by eq. (2): if the temperature \( T_w \) increases, the atomic density \( N_{\text{at}} \) must increase to compensate the decreasing term \( \sqrt{T_w}\exp(E_A/k_BT_w) \) and maintain the density of adatoms constant. This is what we observe in fig. 2(b), where the threshold at \( T_w = 215 \)°C is obtained for an atomic density larger than the one necessary to reach the threshold at \( T_w = 190 \)°C.

We now analyse in more details the radiative equation (eq. (1) for \( N_I(t) \)). Unlike the thermal neutral atoms, the ion flux toward the surface is very different from the flux of the “chemisorbed” atoms escaping from the surface: as stressed before (see footnote \(^2\)), the desorption term in the radiative equation has been measured to be much smaller than the adsorption one and can be neglected. The adsorption term is the product of the ion flux close to the surface and the probability \( p_I \) that an ion will be neutralized on the surface. The ion flux itself is proportional to the flux of excited atoms and to their two-photon ionization rate:

\[
\frac{dN_I}{dt} = p_I \sigma_2 g(\delta) \frac{I^3}{\hbar \omega^2} \sqrt{\frac{k_BT_w}{2\pi\hbar}} \pi^2 n_A, \tag{3}
\]

which is consistent with our observation that this contribution is proportional to the atomic density and has a cubic dependence on the laser intensity for constant \( p_I \). In eq. (3), \( \sigma_2 \) is a generalized cross section for two-photon absorption, \( \tau \) is the lifetime of excited atoms, \( \delta \) is the laser detuning in relation to the D\(_2\) central frequency and \( \sigma_1(\delta) \) is the cross section for absorption by a ground-state atom. In \( \sigma_1(\delta) \) the Doppler-broadening effect of atoms in motion is taken into account. The factor \( g(\delta) \) incorporates the resonant dip due to the surface quenching of excited atoms [14] (see fig. 3(b)).

A simple model of the interaction between a solid surface and a singly charged ion makes explicit the dependence of the probability \( p_I \) [25] on the coverage-dependent work function of the substrate [23] \( \phi(\theta) = \phi_0 - \gamma \theta \) and the consequent threshold behaviour:

\[
p_I = \frac{\sum \lambda [T_{\tilde{a}}^{0}]^2 L(\epsilon_G, \epsilon_a, \Delta) f(\epsilon_G, \epsilon_F, T_w)}{\sum \lambda [T_{\tilde{a}}^{0}]^2 L(\epsilon_G, \epsilon_a, \Delta)} , \tag{4}
\]

where \( p_I \) is the product of \( T_{\tilde{a}}^{0} = \langle a|V|\tilde{k}\rangle \), the transition probability of an electron from a surface level \( |\tilde{k}\rangle \) to a vacant atomic level \( |a\rangle \), the surface Fermi distribution \( f(\epsilon_G, \epsilon_F, T_w) \) at temperature \( T_w \) and the atomic line shape \( L(\epsilon_G, \epsilon_a, \Delta) \), of width \( \Delta \), that we approximate by a Dirac delta function at the energy \( \epsilon_a \) of the vacant atomic level. With such simplifications we obtain

\[
p_I = \frac{1}{1 + \exp((\phi_0 - |\epsilon_a|) - \gamma \theta)/k_BT_w} , \tag{5}
\]

where \( \phi_0 \) is the work function of the clean surface and \( \gamma \) is a proportionality coefficient. The range of Cs coverage in which \( p_I \) significantly varies is very narrow (see fig. 4(c)). The order of magnitude of the difference \( (\phi_0 - |\epsilon_a|) \) is a few eV for an alkali atom close to a clean metallic surface [26]. For our experiment, \( p_I \) can be assumed to be a constant (saturated value) almost immediately above the threshold density, so that the film growth rate varies linearly with the atomic density as observed (figs. 2(a))
and (b)). We thus interpret all of the features observed during the Cs film growth on our cell’s window. Fits of the growth rate as a function of the atomic density, with eqs. (1)–(5), are shown in figs. 2(a) and (b). The fixed parameters in each case are the experimental values of the intensity, of the window temperature and of the atomic density, as well as $\gamma = 20 \text{eV}$ (from [23]) and $(\phi_0 - |\epsilon_a|) = 4 \text{eV}$ (from [20]) in eq. (5). The adjustable parameter is $\sigma = (dN_I/dt)/(p_I n_A F^2)$. Using a typical measured rate of film growth, $dL/dt \approx 4 \times 10^{-3} \text{nm/s}$, we estimate the adsorption rate of ions at these intensities to be on the order of $10^{11}$ atoms/s on the illuminated surface. The fits yield values of $\sigma$ on the order of $10^{-2} \text{J}^{-3} \cdot s^2 \cdot \text{cm}^7$. The functional dependence of the fits on the parameters is consistent with the experimental measurements. A detailed quantitative analysis of the process, and particularly the estimation of the effective ion yield in the vapour, depends on a systematic study of the function $g(\delta)$ for a given material of the window.

In conclusion, we have identified the sequence of vapour and surface processes leading to the formation and growth of a light-induced thin metallic film at the interface between a transparent dielectric solid and an alkaline vapour. Preliminary results show that the structure is very stable, provided that the window temperature is quickly lowered after the pump laser is switched off. In addition to its technological appeal [27], this film growth technique also provides a method of characterizing various aspects of the interaction between a dielectric surface and gas phase atoms, particularly the adsorption time and energy and the caesium-induced lowering of the work function in dielectric substrates. Further spatial study of the film growth may also provide insights into effects neglected in this work, such as dark- or light-induced diffusion on the surface.

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We acknowledge support from FINEP, CNPq and CAPES (Brazil). We warmly acknowledge J. W. R. Tabosa for carefully reading the manuscript.

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