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Friction reduction of Ne monolayers on preplated metal surfaces

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With a quartz-crystal microbalance technique we have studied the nanofriction of Ne monolayers at temperatures below 6.5 K and in ultrahigh-vacuum conditions deposited on metallic surfaces plated with heavy rare-gases multilayers. Covering the electrode with one layer of Kr or Xe increases the slippage of a Ne monolayer by a factor close to 3. Such a behavior has been observed with smooth lead electrodes as well as with rougher gold ones. The lubrication effect does not improve with thicker overlayers.

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I. INTRODUCTION

Recent advances in theoretical modeling[1,2] and experimental probes[3] have provided not only a significant improvement in our understanding of atomic friction but also new prescriptions to control friction and wear at the nanoscale. Actually, as the size of the system decreases, the effects of friction and wear become so much amplified by the increase in surface-to-volume ratio that they represent one of the main limitations to the commercialization of microelectromechanical devices. The enhanced contribution of these interfacial phenomena cannot be tackled by adopting the machinery which works well in the macroscopic world because there are no simple microscopic analogs of gears and bearings and adding fluid lubricants is not possible because either the microstructures collapse to capillary forces in the presence of liquids or the lubricants become too viscous when confined in very small gaps.

One effective way to reduce friction at a dry micro/nanocontact involves the sliding of two incommensurate crystalline surfaces.[4] The underlying idea of this phenomenon is that the forces coming from the mismatched atoms in the contact area point in all directions and sum up to zero. Vanishing friction between a graphite flake sliding over a graphite substrate was found when the two graphite surfaces were rotated out of the commensurate locking angle.[5] Evidence of a possible structural depinning was also observed in a quartz-crystal microbalance (QCM) study of Ne monolayers deposited on lead at low temperature.[6] At small coverages, the Ne film is in a fluid phase that at such low temperatures is locked to the substrate. As the film coverage increases, small islands start to form. Close to about 0.4 layers, some incommensurate solid islands, which are weakly bound to the surface, start to slide.

Previous experiments suggest that preplating a surface may also increase the slippage of adsorbed monolayers. QCM measurements of He multilayers on graphite down to 0.35 K show a slip time τ (see Sec. III) between the first layer and the graphite surface of about 10 ns and much larger values, on the order of 100 ns, between the second and first layer.[7] However, these results were obtained by modeling the QCM response assuming that each layer of helium (i) behaves independently from each other and (ii) slides above that underneath. In another QCM study,[8] the sliding friction of Ar on silver preplated with one or two Xe layers was investigated at 77 K. It was found $\tau = 1.5$ ns for one Ar layer on bare Ag, which increased to ~4 ns on Ag plated with one or two Xe layers. In this latter case, τ was calculated under the assumption that changes in QCM response upon Ar uptake were entirely attributable to slippage at the Ar-Xe interface.[8] However, a quantitative interpretation of this experiment is not easy because at 77 K both Xe and Ar are quite active both thermodynamically (e.g., they have non-negligible vapor pressures which may cause mixing of the two adsorbates) and dynamically (they both slide with comparable τ on gold).

Hereafter, we present an extensive QCM study of the sliding of Ne monolayers on metal surfaces preplated with Kr and Xe films of different thickness at temperatures ~6.5 K, whose results provide direct and unambiguous evidence of a pronounced reduction in the sliding friction on the coated surfaces. This paper is organized as follows. First, we describe in some detail the setup used for these measurements pointing out the technical improvements it presents with respect to other experiments. We then describe the friction data acquired on lead and gold surfaces, both bare and coated with Kr and Xe multilayers, before discussing possible interpretations of the data in the conclusions.

II. EXPERIMENTAL SETUP

The microbalance is a small quartz disk whose principal faces are optically polished and covered by two metallic films, which are used both as electrodes and as adsorption surfaces. Lead is chosen as a material for the electrodes because it is easy to: (i) grow a very uniform film already at room temperature and (ii) remove the surface contaminants deposited over time on the electrodes after a mild sputtering treatment, thanks to its large diffusion coefficient. The Pb electrodes have been grown in UHV conditions (base pressure $<10^{-8}$ mbar) by using a magnetron source. The substrate was a blank quartz with a resonance frequency of 5 MHz polished down to an rms roughness of about 0.3 nm. Prior to Pb evaporation, the quartz substrate was cleaned and annealed under UHV conditions. In order to avoid the formation of three-dimensional clusters, elevated deposition fluxes (in the range of 20 nm/sec) were chosen while the sample was maintained at room temperature. For the different samples produced, the thickness was in the range 50–150 nm. The resulting Pb film morphology is quite similar to that previously reported:[6] (111) terminated flat terraces are present in a large percentage with a typical size in the range 20–100 nm. The rms roughness is of 3 nm measured over an area of $2\times 2\ \mu\text{m}^2$. We have also used a quartz with gold electrodes thermally evaporated by a specialized company (Laptech Inc.).

At resonance, the two parallel faces of the QCM oscillate in a transverse shear motion. The condensation of a film on the electrodes is signaled by a decrease in the resonance frequency. Any dissipation taking place at the solid-film interface is instead detected by a decrease in the corresponding resonance amplitude.[9] The resonance frequency and amplitude are measured by means of a frequency modulation technique in which the output signal of a radio-frequency generator is locked onto the peak resonance.[10] The quartz crystals used in this study had a fundamental frequency $f=5$ MHz with a quality factor of about 90 000 at low temperature. In these conditions our setup guarantees a stability in the resonance frequency of about ± 0.1 Hz while that in the amplitude is approximately $\pm 0.1\%$. The QCM is mounted in an UHV system[11] specifically designed for QCM experiments that comprises the main chamber housing the sample holder and a fast-entry load lock system provided with a sputtering-ion gun to clean the electrodes from surface contaminants. Unlike other experiments in which the film covering the QCM is obtained by admitting a known amount of gas at high temperature and then cooling down the sample cell to the base temperature,[7,12,13] in our setup the film is condensed directly onto the QCM, kept at the chosen low temperature, by slowly dosing high-purity gas through a nozzle facing the quartz electrode. The deposition rate can be varied by acting on the sapphire leak valve. Typical rates are comprised between 20 and 90 min for the deposition of one nominal layer. No systematic difference in the QCM response is observed among measurements comprised in this ample time interval, suggesting that the data is taken under near equilibrium conditions.

III. EXPERIMENTAL RESULTS

Figure 1 shows representative isothermal QCM scans indicating the slip time τ as a function of the coverage of Ne films deposited on bare Pb at 6.5 K. In the absence of a vapor,[14] the slip time, which describes the viscous coupling between the substrate and the film, can be easily calculated from the shifts in the resonance frequency and amplitude of the QCM.[9] It represents the time constant of the exponential film velocity decrease due to an hypothetical sudden stop of the oscillating substrate. Very low τ mean high interfacial viscosity and, in the case of a film rigidly locked to the substrate, τ goes to zero. For the determination of the film thickness, we have assumed an areal density for the completion of one Ne monolayer[6] of 0.12 atoms/Å^2. The frequency shift for the deposition on one QCM electrode of a Ne layer is then 2.3 Hz. The data stop at about one layer because at higher coverages desorption effects start to become important. The various curves correspond to measurements taken in different cool downs and/or days and refer to a very ample range of deposition rates. The continuous line is the average of the different scans with the error bars indicating the calculated normal dispersion. The data at very small coverages, <0.06 layers, are not shown because affected by a large scatter. The Ne results show a τ practically zero at low coverages, while above ~ 0.3 layers it is distinctly different from zero and reaches a value of ~ 3 ns at monolayer completion, a typical value for rare gases adsorbed on metal surfaces.[12,15,16] This behavior is similar to that we have reported in a previous study,[6] as described in Sec. I.

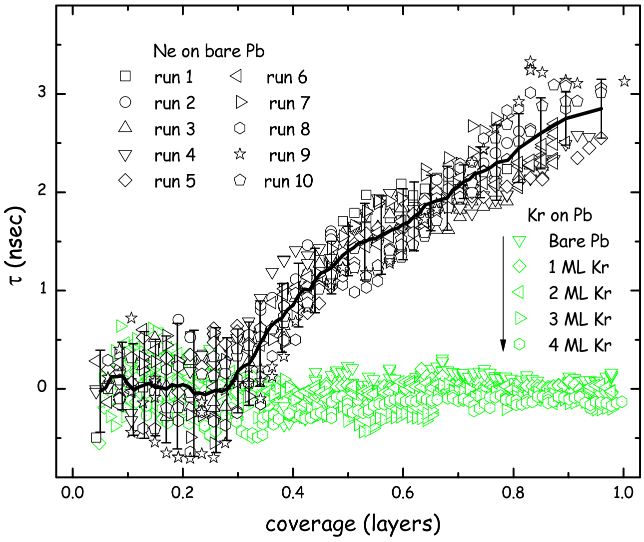

FIG. 1. (Color online) Slip time of Ne on bare Pb corresponding to isothermal runs (1 to 10) taken at 6.5 K in different days and/or cool downs (black symbols). Black solid line is the average over the performed runs. Slip time of individual Kr layers deposited on Pb coated with Kr multilayers of increasing thickness (from 0 to 4 monolayers) (green symbols).

We have then studied the slippage of Ne films on Pb plated with Kr films of nominal thickness ranging from 1 to 5 layers. For the areal density of a solid Kr layer we have used the value of 0.078 atoms/Å^2 derived from bulk data.[9] We point out that the classification in terms of number of Kr layers is used just for convenience. In fact, scattering experiments on the adsorption of rare gases on metal surfaces suggest that the film grows layer by layer for the first two, three layers followed by bulk growth.[17] Figure 1 also displays τ measured during the individual depositions of the five Kr layers. The data shows a null slip time suggesting that the Kr layers are rigidly coupled to the quartz electrode. There are two possible and concurrent reasons explaining such a behavior. First of all, the small force of inertia acting on the Kr atoms induces a slow, thermally activated motion of the adsorbate along the electrodes oscillating direction, with the activation barrier being the amplitude of the corrugation of the surface potential energy.[18] *Ab initio* calculations of the adsorption of rare gases on metal surfaces show that the corrugation felt by the adsorbed atoms increases with the atomic

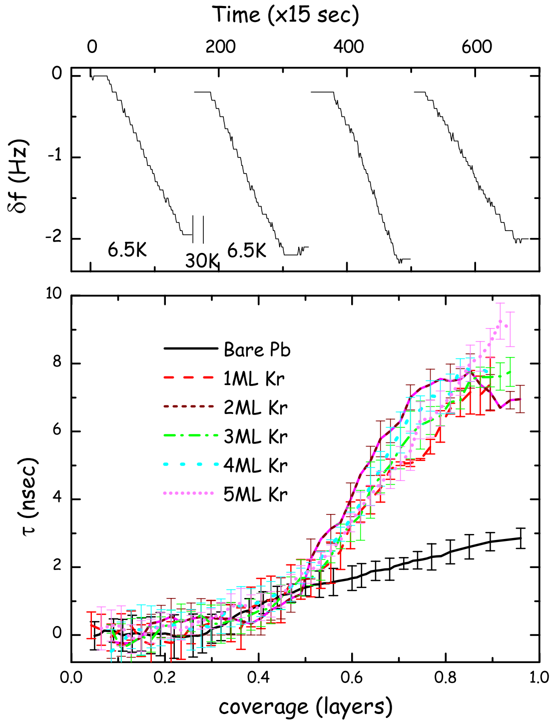

FIG. 2. (Color online) Top: frequency changes corresponding to successive Ne depositions on Pb covered with four Kr layers. Bottom: slip times of Ne monolayers on bare Pb (solid line) and Pb covered with Kr layers of increasing thickness (dashed lines). Each curve represents the average of at least four isothermal scans.

number.[19,20] Accordingly, a decrease in the bath temperature may significantly lower the mean drift velocity of the Kr film. Another important factor is the pinning of the adsorbate due to the unavoidable surface defects, whose strength is related to the binding energy of the adsorbate and whose effects are very much amplified at low temperatures.[21,22] This agrees with the observation[12] that N_2 films are highly susceptible to become pinned below 10 K and with previous studies[23] in our laboratory that indicate that only Ne consistently slides at these low temperatures, all the other heavier adsorbates such as Ar, Kr, Xe, and N_2 being pinned.

The main graph of Fig. 2 shows the mean τ derived from repeated Ne isothermal depositions, four at the least, on Kr layers of different thickness. After each Ne deposition, the system was warmed up to 30 K, a temperature sufficient for the complete removal of the Ne atoms but not of the Kr film. The top plate of Fig. 2 reports a sequence of four successive Ne depositions on Pb covered with four Kr layers. It displays the frequency change $\delta f = f - f_0$, f_0 being the initial resonance frequency, as a function of the number of data acquisitions which is equivalent to time, each point corresponding to about 15 s. The overall vertical shift is equivalent to the deposition of a full Ne monolayer. The breaks in the graph are due to the warming up cycles. It is evident that the frequency goes back, within ±0.3 Hz, to the initial value and no monotic increase is observed, confirming that the Kr overlayer has not been affected by this cleaning procedure. In general, after each warm up the resonance parameters are reproducible within ±1 Hz for the frequency and within ±0.5% for the amplitude. The isothermal scans of Fig. 2 indicate that covering the Pb surface with a Kr film significantly increases the slip time of the Ne atoms. Again, no slippage is observed for Ne coverages less than ∼0.3 layers on the plated Pb, suggesting that the depinning mechanism remains the same. Above this threshold, τ progressively increases and near the completion of a Ne layer becomes three times larger than the corresponding value measured on the bare Pb electrode. Interestingly, no observable variation is found on the various Kr layers, indicating that one Kr layer is sufficient to effectively "lubricate" the metal surface.

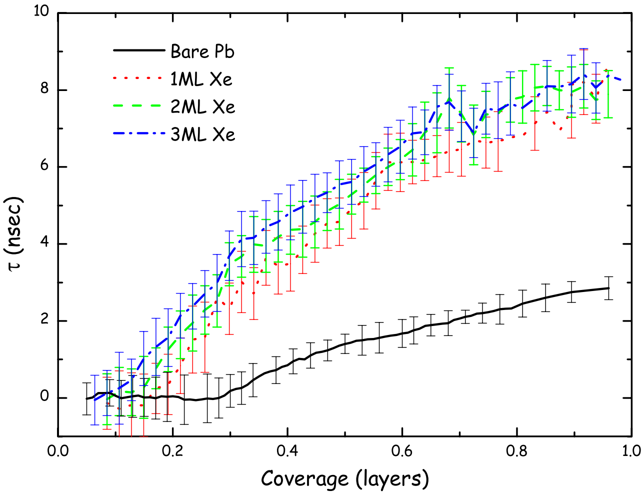

FIG. 3. (Color online) Slip times of Ne monolayers on bare (solid line) and Pb covered with Xe layers of increasing thickness (dashed lines).

Similar behavior is observed if the Pb surface is preplated with a Xe overlayer having a varying thickness comprised between 1 and 3 ML. The expected frequency shift of 7.3 Hz for the completion of a solid Xe layer on Pb(111) has been determined using an areal density[24] of 0.06 atoms/Å^2. As before, the deposition of Xe does not change the QCM amplitude, a result to be expected given the larger surface corrugation experienced by a Xe atom with respect to Kr.[19,20] Figure 3 compares the Ne slip times measured on Xe with those on bare Pb. The depinning now occurs at a smaller coverage, ∼0.15 layers. This decrease may be related to the different periodicity of the Xe surface potential, although detailed modeling is required to confirm it. The slip time near the completion of a Ne monolayer is instead practically the same as that measured on Kr. Again, no further increase in the slip time is observed above one Xe layer.

Finally, we have studied the slippage of Ne monolayers on a QCM with gold electrodes. Figure 4 shows the measured τ on bare Au(111) and on gold preplated with Kr films of different nominal thickness. The datapoints were taken at the third overtone of a 5 MHz plate because the fundamental mode had a very small quality factor. They confirm the behavior displayed in Fig. 2. Interestingly, the slip times are now much smaller, by a factor ∼100, than those found on Pb. The noise in the gold data reflects the very small values of the slip times which correspond to a tiny relative decrease in the resonance amplitude of only ∼0.5% for one Ne layer.

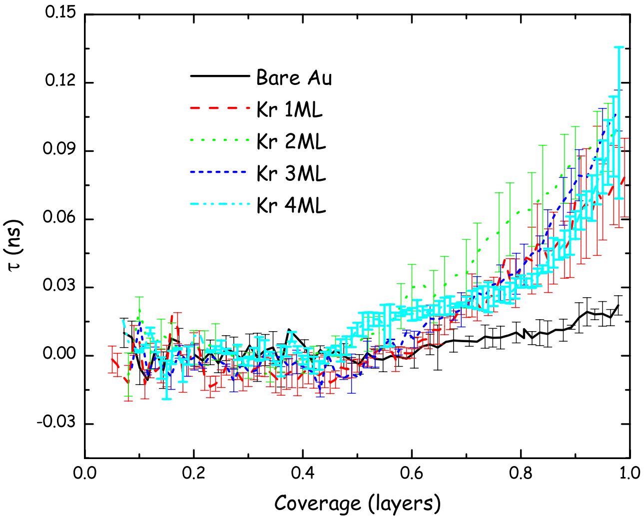

FIG. 4. (Color online) Slip times of Ne monolayers on bare Au (filled line) and Au covered with Kr layers (dashed lines) of increasing thickness.

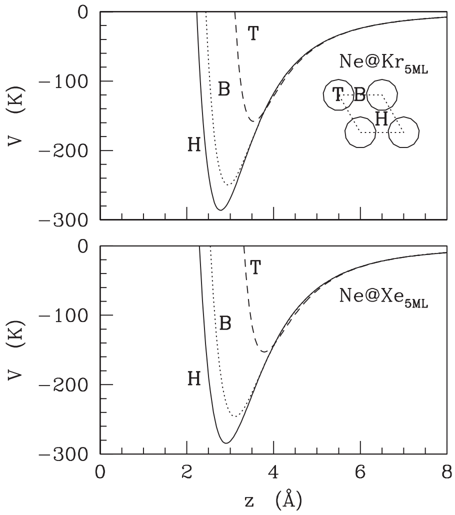

FIG. 5. Potential-energy curves for a Ne atom interacting with a five-layer film of Kr (upper panel) and Xe (lower panel), as a function of the Ne-surface distance. Inset: classification of the adsorption sites: hollow (H), bridge (B), and top (T).

IV. DISCUSSION AND CONCLUSIONS

The Ne results on the plated metals cannot be explained in terms of boundary friction with the Kr (Xe) overlayer acting as a lubricant of nanometric thickness because, as we have just seen, the Kr (Xe) film is dynamically inert at these low temperatures: it is just a solid rigidly coupled to the metal surface. In past adsorption studies, coating a surface, generally graphite, with a simple gas overlayer was found to be an effective way to control the thermodynamics of quantum films.[25,26] This study suggests that this surface functionalization also affects the dynamical properties of an adsorbed film.

Different factors may contribute to the observed behavior. The phononic contribution to the slip time is found to strongly depend on the corrugation of the surface potential.[16] Accordingly, the increased slippage of Ne on the plated Pb would imply that the Kr (Xe) overlayer reduces the strength of the surface potential experienced by the Ne atoms. Unfortunately, no data of the Ne/Pb surface potential exist to validate or deny such an explanation. The fact that Ne slides more easily on the insulating Kr (Xe) overlayer rather than on lead may also suggest that the electronic contribution to friction cannot be neglected.[8] However, at 6.5 K lead is a superconductor, as also confirmed by the pick-up signal measured between two Meissner coils mounted across the QCM, and therefore the electronic dissipation channel should be frozen out as on an insulator. Concerning this specific point, we add that recent measurements of Ne films on bare Pb carried out across the superconducting to metal phase transition do not show any extra dissipation which can be attributed to electronic friction.[27] Finally, one must consider that the surfaces are not ideal and that the pinning effects[21,22] due to the presence of defects may change between bare and plated Pb.

In order to explain why Ne behaves similarly on Kr (Xe) multilayers, we have computed the potential felt by an isolated Ne atom adsorbed on a Kr (Xe) film. We assume for simplicity that the structure of the multilayer is bulklike and that its orientation is such that the (111) surface is exposed to the adsorbed Ne atom. We consider a number of layers in the Kr (Xe) film ranging from 1 to 5. The Ne potential energy is calculated by direct summation of the pair Ne-Kr (Ne-Xe) interaction, as a function of the Ne atom-substrate distance, for three different adsorption sites: the top (T) site just above a surface Kr (Xe) atom, the hollow (H) site at the center of the triangle formed by three neighboring surface atoms, and the bridge (B) site between two adjacent surface atoms (see also inset in Fig. 5). We have used in our calculations the Ne-Kr and Ne-Xe pair interactions from Ref. 28. The calculated potential curves for a five-layer film of Kr (Xe) are shown in Fig. 5. They appear to be very similar for Kr and Xe, which is a direct consequence of the similar well depths in the Ne-Kr and Ne-Xe pair potentials, equal to 70.7 K and 71.8 K, respectively.[28] Our results show that the energy barriers separating two adjacent lowest-energy H adsorption sites across a B site (calculated using a five-layers film), is about 40 K for both Kr and Xe substrates, while is about 130 K, again for both Kr and Xe, across a T site. The potential minima amount to 285 K for both layers. We also find very small differences in the Kr (Xe) surface potential for film thicknesses greater than two layers. For thinner Kr (Xe) films, the relative difference in well depth and corrugation with respect to the asymptotic values is less than 10%. In these calculations the effect of the underlying Pb substrate is neglected. This has no consequences on the calculated barriers for the thick multilayers; for 1–2 layer films the presence of the Pb substrate is expected to increase slightly the overall binding energies of the film but most likely will not affect the corrugation amplitudes. All of this is consistent with our QCM results on the multilayers.

Finally, it is tempting to explain the difference in the data on gold and on lead as an evidence of a diverse electronic contribution to friction between a metal and a superconductor.[8,12] However, not only the chemistry (e.g., surface potential) but also the surface morphology is different in the two cases, the average size of the gold crystallites being smaller than that of the lead terraces. Actually, an analysis of the gold profile by means of a scanning tunnel microscope reveals a very high density of atomic steps, due to the strong predominace of small terraces with sizes well below 10 nm.

In summary, we have observed increased slippage of Ne over metals plated with Kr (Xe) multilayers with respect to the bare surfaces. The “lubricating” action of the multilayers increases the slip time by a factor ~3 for a Ne layer. One Kr (Xe) layer is sufficient to guarantee such an effect. Detailed modeling based on reliable surface potentials is required to elucidate the physical mechanisms behind this effect.

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