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Atomic-Scale Friction in Xe/Ag and N_2/Pb [1]

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Quartz crystal microbalance (QCM) and electrical resistivity measurements were carried out on the systems Xe/Ag and N_2/Pb to determine the relative contributions of electronic and phonon dissipative mechanisms to sliding friction. Results show significantly differing proportions of electronic friction in the two systems.

KEY WORDS: electrical resistivity; lead; nanotribology; quartz microbalance; silver; superconductivity; xenon.

1. INTRODUCTION

The fundamental origins of friction, an important physical phenomenon in light of both its everyday familiarity and its enormous economic impact, have been discussed and debated for at least 300 years, with very little resolved [1]. With the advent of new experimental techniques capable of studying the force of friction which results when a finite number of atoms is made to slide on a crystalline substrate, a new field involving investigations at atomic length and/or time scales (nanotribology) has evolved [2, 3] allowing frictional dissipative mechanisms to be probed for the first time [4].

At the atomic scale, friction is believed to originate primarily via sliding induced excitation of atomic lattice vibrations (phonons) [1], whose lifetimes are of the order of 10^{-9} to 10^{-12} s. Electronic contributions to the energy dissipation (attributed to conduction electron scattering from surface impurities) have also been suggested as significant contributors to frictional energy losses, if conducting materials are involved [5].

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Definitive proof of electronic contributions to friction is of great interest, since to date the vast majority of fundamental theoretical treatments of friction have considered phonon contributions only [1]. A variety of practical applications becomes possible, moreover, in cases where electronic contributions dominate. For example, for the case of adsorbed films or particles on metal substrates, the atoms could be dragged along the surface via electronic friction forces arising from an electrical current. Qualitative evidence for the occurrence of electronic contributions to friction has been previously demonstrated for the case of ethane and ethylene films adsorbed on silver and chemisorbed oxygen surfaces [6]. Quantitative comparison with theory was difficult, however, for those studies due to the fact that the structure of chemisorbed oxygen on silver is sensitively dependent on kinetic details [7].

Two experimental approaches to determine the relative contributions of electronic and phononic dissipative mechanisms to sliding friction in metallic interfaces involve (a) comparison of electrical resistivity data with that recorded via a quartz crystal microbalance (QCM) technique and (b) QCM measurements of friction levels above and below the superconducting transition temperature of a metal substrate. We employed the first technique on the system Xe/Ag(111) and the second technique on the system N_2/Pb and report our observations here.

2. EXPERIMENTAL

The quartz crystal microbalance (QCM) has been used for decades for microweighing purposes [8] and was adapted for friction measurements in 1986–1988 by Widom and Krim [9, 10]. A QCM consists of a single crystal of quartz which oscillates in transverse shear motion with a quality factor Q near 10^5. Adsorption onto the microbalance produces shifts in both the frequency f_o and the quality factor Q, which are indicative of the degree to which the adsorbate is able to track the oscillatory motion of the underlying substrate. Characteristic slip times, τ, and friction coefficients (i.e., shear stresses per unit velocity) η, are determined via the relations [9]

$$\delta(Q^{-1}) = 4\pi\tau\,\delta f_o, \qquad \eta = \frac{\rho_2}{\tau} \tag{1}$$

where ρ_2 is the mass per unit area of the adsorbate. In terms of separate phonon and electron-hole slip times, τ_{ph} and τ_{eh}, the slip time τ can ideally be written as

$$\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{eh}} \tag{2}$$

3. RESISTIVITY MEASUREMENTS

One potential approach to determining the electronic contribution to the total sliding friction in a film–metal interface assumes that the conduction electrons in the metal substrate experience a drag force equal in magnitude to the force required to slide the adsorbed film [5]. The change in the metal film's resistivity ρ due to adsorption of the monolayer has been related to the electronic slip time τ_{eh} via the expression [5]

$$\frac{1}{\tau_{eh}}=\frac{n^2e^2}{M}t\frac{\Delta\rho}{\Delta n_a} \tag{3}$$

where n is the volume density of conduction electrons, e the electronic charge, M the mass of an adsorbate particle, t the metal film thickness, and n_a the number of adsorbate particles per unit area. Values of τ_{eh} for a range of chemisorbed and physisorbed systems have been tabulated in Ref. 5, with physisorbed systems characterized by τ_{eh} in the range 10^{-9} to 10^{-10} s. By comparing the value of τ_{eh} determined from resistivity measurements with the value of τ determined from QCM measurements, one can, in principle, determine the relative contributions of phonon and electron dissipative mechanisms to friction.

Data were recorded in equilibrium conditions for adsorption of Xe onto the surface of silver film electrodes which were evaporated *in situ* onto overtone polished quartz crystals ($f_o = 8$ MHz). The evaporation was carried out at room temperature with 99.999% pure Ag at a deposition rate of 0.05 to 0.1 $\text{nm}\cdot\text{s}^{-1}$. In the case of the resistivity measurements, a four-wire pattern was evaporated onto the quartz crystal surface. For QCM measurements, a silver electrode was evaporated onto each major face of the quartz crystal by rotating the sample between depositions. The samples were then transferred, within the vacuum system, to a gas adsorption chamber where adsorption could be carried out at 77.4 K.

Figure 1 shows resistivity and QCM data for adsorption of Xe onto a 95-nm-thick Ag film at 77.4 K. The frequency shift data reflect the number of adsorbed particles per unit area, while the amplitude data indicate the increase in dissipation levels upon adsorption of Xe layers. Each step in the frequency shift trace corresponds to condensation of a monatomic solid layer of Xe, and the verticality of the steps is indicative of large ($\approx$100-nm) regions of substrate crystalline uniformity. The resistance data show the resistivity of the silver film increasing monotonically with the frequency shift for coverages up to one monolayer and achieving a saturation value beyond it. This behavior is consistent with resistivity measurements reported previously [11].

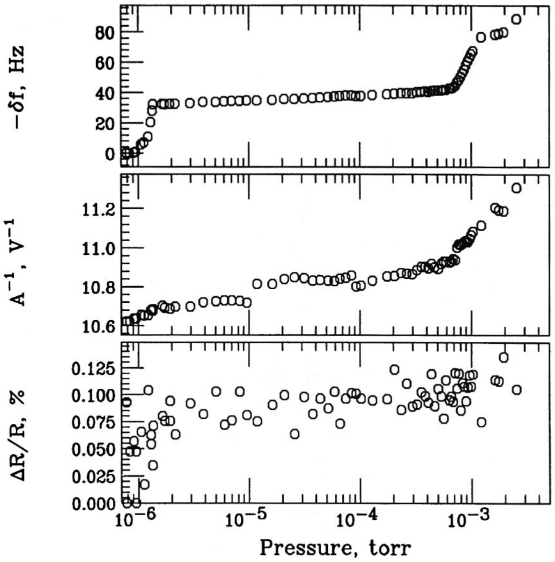

Fig. 1. QCM frequency and amplitude shifts and resistance data versus vapor pressure for Xe/Ag at 77.4 K.

The inverse of the electronic and total slip times calculated from the Fig. 1 data set, which are proportional to the electronic and total sliding friction, respectively, are presented in Fig. 2 versus coverage. One monolayer of compressed Xe is defined as 0.0597 atoms $\cdot$ $Å^{-2}$. Because of large uncertainties in the data below half-monolayer coverages, we are careful not to make any conclusions in this region. Detailed analysis of Xe/Ag isotherms is discussed in Ref. 12. A key feature to note here is the sharp decrease in the inverse total slip time during the compression of the xenon film monolayer, which has been reasonably attributed to phonon effects in the film during its compression [12]. Indeed, the electronic slip time remained essentially unchanged throughout the compression regime.

Moreover, looking at the shear stress, which is proportional to coverage/sliptime, from the first monolayer (0.0597 atom $\cdot$ $Å^{-2}$) to the second monolayer (0.1194 atom $\cdot$ $Å^{-2}$) we see that the shear stress associated with the total slip time increases with the coverage. That associated with the electronic slip time does not, since the rise in coverage is canceled out by the decrease in inverse slip times. This is consistent with the fact that electronic friction arises from interfacial electronic interactions and is therefore determined primarily by the first layer. On the other hand, phonon friction associated with a bilayer can potentially be much greater

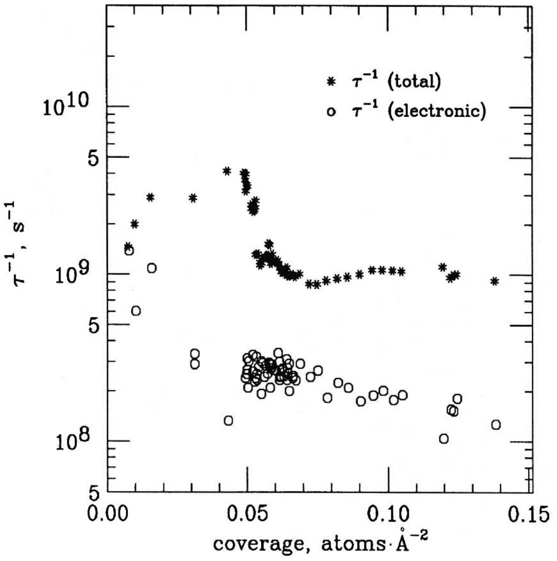

Fig. 2. Typical values for the inverse of the electronic and total slip times, τ_{el} and τ, for Xe monolayers adsorbed on Ag(111).

than that associated with a monolayer, due to the presence of more vibrational modes into which mechanical energy can be dissipated [13].

Comparison of the electronic and total slip times indicates that electronic friction, based on Eq. (3), is at most 30% of the total friction, suggesting that phonon effects are the dominant mechanisms in the sliding friction for the system.

4. SUPERCONDUCTIVITY MEASUREMENTS

Another approach to determine the electronic contribution to the total sliding friction is to see how the slip time τ changes when the metal substrate undergoes a phase transition to its superconducting state, in which case the electronic contributions should be significantly altered, with $1/\tau_{el} \rightarrow 0$, leaving only phonon contributions.

Experiments were carried out on the system N_2/Pb. Pb thin films are known to become superconducting as high as 7.5 K. We evaporated 200-nm-thick lead films onto quartz crystals for QCM and electrical resistivity measurements. Evaporation was performed at room temperature and at a base pressure of 10^{-8} Torr. The samples were then transferred to a gas-dosing chamber where measurements can be carried out down to 4.2 K.

Figure 3 shows QCM data for both bare and nitrogen-covered Pb films. Resistivity data are also included to show that the samples did become superconducting. As expected the QCM inverse amplitude, proportional to the energy dissipation, for the nitrogen-covered metal film is shifted up relative to that for the bare sample indicating higher dissipation levels due to slippage between the gas layers and the film. The resistance, however, shifted opposite the expected direction. It is likely that the lead film may not have been smooth enough for Eq. (3) to be valid. Although it would be preferable to repeat the experiment with higher-quality samples, the data obtained from the QCM measurements, which do not require atomically flat surfaces, are sufficient for the purpose of comparing dissipation levels for nitrogen sliding on superconducting lead and on normal lead.

Figure 4 shows QCM and resistance data for the case where adsorbed nitrogen is present. The sample becomes superconducting at time = 2200 s (a temperature of 6.6 ± 0.1 K was recorded by a thermometer attached to the chamber wall) and returns to normal around time = 2500 s (7.2 ± 0.1 K). The lower transition temperature recorded at 2200 s is

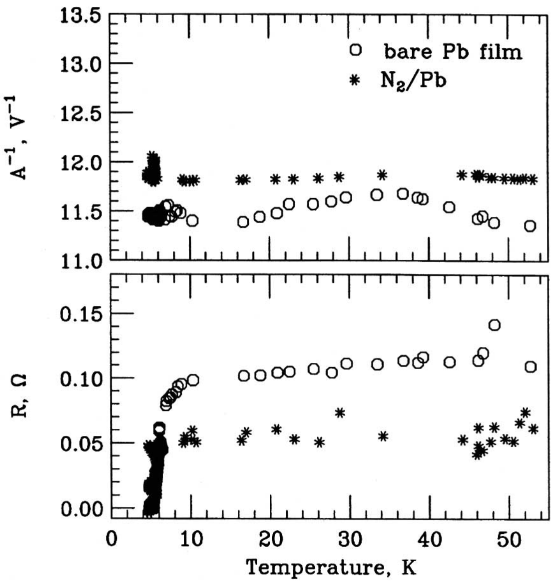

Fig. 3. Inverse QCM amplitude and resistance data versus temperature for bare and nitrogen-covered lead films.

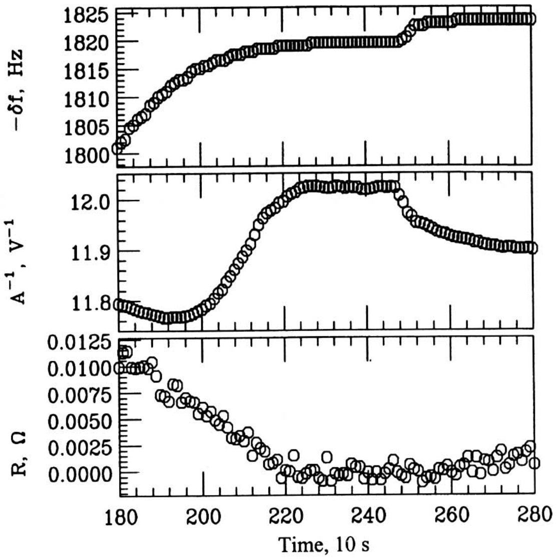

Fig. 4. QCM and electrical resistivity data for N_2/Pb. Data are plotted against time for clarity.

attributed to a difference in the rates of cooling between the thermometer and the sample during a very fast cool-down process, whereas the warm-up process occurred under much slower conditions. When the film is superconducting, the amplitude trace exhibits higher dissipation levels. This behavior is not observed for the bare samples. The additional energy dissipation can be attributed to an increase in slippage between the film and the substrate as interfacial friction levels go down due to the disappearance of electronic contributions when the substrate becomes superconducting.

As the lead film returns to normal, an increase in $-\delta f$ is observed. We attribute this frequency shift to slippage effects since no physical argument can justify an increase in coverage at this point. The expected corresponding decrease in $-\delta f$ when the sample enters superconductivity is not discernible, perhaps because this transition occurred during the faster cool down process.

Comparing the relative dissipation levels when the lead is superconducting (when electronic contributions may be negligible), $\propto \delta(A^{-1}) \approx 0.60\ V^{-1}$, with those when the lead is in its normal state (when both electronic and phononic contributions are present), $\propto \delta(A^{-1}) \approx 0.45$ V, we estimate phonon contributions to sliding friction to be about 25%. This indicates that electronic effects dominate over phonon mechanisms for this case.

5. DISCUSSION

We have carried out electrical resistivity and QCM measurements on the systems Xe/Ag(111) and N_2/Pb to determine the relative contributions of electronic and phonon dissipative mechanisms to sliding friction. Our results show the proportion of electronic contributions to be around 30% for Xe/Ag at 77 K, and 75% for N_2/Pb at 7 K. While there is a striking difference in the dominance of electronic effects in the two systems, it is clear that electronic mechanisms are a significant source of energy dissipation.

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