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TESI DI DOTTORATO

FRICION PROPERTIES OF
HOMOGENEOUS AND MICROPATTERNED
SURFACES

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Abstract (Italiano)

I fenomeni legati alla tribologia quali adesione, attrito e usura si manifestano quando due solidi vengono messi in contatto. Come le dimensioni dei dispositivi si riducono alle micro- e nanoscale, il rapporto superficie-volume aumenta e gli effetti dovuti alle forze di attrazione tra corpi (gravità e inerzia) diventano insignificanti rispetto a quelle superficiali (van der Waals, capillari, elettrostatiche e legami chimici). A queste scale, l’uso di lubrificanti liquidi ed i sistemi macroscopici di riduzione dell’usura sono inefficaci. Nei sistemi microelettromeccanici (MEMS) le forze di attrito e quelle statiche d’interfaccia sono comparabili con le forze che muovono il dispositivo. Nuove strategie devono, quindi, essere messe a punto per ridurre i fenomeni di attrito.

In questa tesi io ho investigato i meccanismi microscopici che regolano l’attrito. Tramite la tecnica della microbilancia a cristallo di quarzo, ho misurato la viscosità interfacciale di monostrati (ML) di gas puri depositati su superfici di piombo (111) estremamente uniformi. Per i film di azoto a temperature sotto i 15K non si osservano effetti di dissipazione, suggerendo che questi film siano rigidamente ancorati alla superficie oscillante degli elettrodi. Aumentando la temperatura fino ai 20K vediamo scivolamento dei film d’azoto per ricoprimenti superiori a circa 0,5 MLs nominali. Un comportamento analogo è mostrato anche dai film di Argon. Per i film di Neon abbiamo invece osservato una marcata transizione di depinning che separa una regione a basso ricorimento superficiale, dove il film è fermamente ancorato al substrato oscillante, da una regione ad alto ricorimento nella quale si osserva scivolamento all’interfaccia solido fluido. Questi dati suggeriscono che nel sistema avvenga un depinning strutturale dei film di Ne solido quando diventano incommensurati con la superficie di piombo. Con questo sistema ho anche studiato il contributo elettronico all’attrito totale attraversando la transizione superconduttiva. I film di Ne non mostrano nessun comportamento anomalo per la dissipazione attorno a Tc.

Con la tecnica della QCM ho anche misurato l’attrito tra i film di Ne e le superfici di oro. Il tempo di scivolamento calcolato per questo sistema era un ordine di grandezza inferiore a quello calcolato per il piombo. Gli effetti dovuti all’accoppiamento tra gli elettroni superficiali e gli atomi adsorbiti potrebbero essere grossi per questo sistema. Allora è stato depositato uno strato isolante di Kr crescente per ridurre
questo accoppiamento. Per ricoprimenti di Kr fino a 2ML è stato misurato un aumento del tempo di scivolamento mentre per ricoprimenti più alti si è osservato un comportamento inverso.

A temperatura ambiente e criogenica è stato svolto uno studio preliminare per valutare lo scivolamento di nanoparticelle di oro del diametro di 15nm depositate su superfici d’oro. Le misure mostrano la inaspettata presenza di scivolamento ad una $T = 5.5K$ su superfici lisce d’oro mentre per superfici rugose è stata trovata una marcata dipendenza dello scivolamento dalla forza esterna applicata.

Infine ho messo a punto una procedura per la realizzazione di superfici di silicio patternate con alchilsilani tramite micro Contact Printing. Gli studi preliminari sull’attrito, condotti con una punta di AFM modificata che presenta sulla base un’area di contatto di circa $2 \times 2\mu m^2$, mostrano una riduzione del coefficiente di attrito per la superficie coperta da OTS di un fattore 2 rispetto a quella di silicio.
Abstract (English)

The tribological phenomena of adhesion, friction, and wear arise when solid objects make contact. As the size of devices shrinks to micro- and nanoscales, the surface-to-volume ratio increases and the effects of body forces (gravity and inertia) become insignificant compared with those of surface forces (van der Waals, capillary, electrostatic, and chemical bonding). In this situation, fluids lubrication and wear mitigation methods are ineffective. In microelectromechanical systems (MEMS), tribological and static interfacial forces are comparable with forces driving device motion. Then new strategies must be employed to reduce friction.

In this thesis I have studied the microscopic mechanisms involved in friction. Using a quartz crystal microbalance technique, I have measured the interfacial viscosity of pure gases monolayers deposited on very homogeneous Pb(111) surfaces. For nitrogen films at temperatures below 15 K, no dissipation is detected, suggesting that the N$_2$ films are rigidly coupled to the oscillating electrode. By raising the temperature close to 20K, we find sliding of the nitrogen film for coverages above about 0.5 nominal layers. Similar behavior is shown by Ar films. For Ne films we have instead observed a pronounced depinning transition separating a low-coverage region, where the film is nearly locked to the oscillating electrode, from a high-coverage region characterized by slippage at the solid-fluid boundary. These data are suggestive of a structural depinning of the solid Ne film when it becomes incommensurate with the lead substrate. With this system I have also studied the electronic contribution to the total friction crossing the superconducting transition of lead. Ne monolayers do not show any anomalous behavior in the dissipation across Tc.

With the QCM technique I have also measured the friction of Ne films on gold surfaces. The calculated slip time was one order of magnitude smaller than for Pb. The effect of the electron coupling with the adsorbate should be high for this system. Then an insulating Kr overlayer was grown on the gold surface to reduce coupling. For Kr coverage lower than 2ML an increase in the slip time was measured while for increasing coverages a reentrant behavior was detected.

A preliminary study of the slippage of 15nm diameter gold nanoparticles deposited on gold has been carried out at room and cryogenic temperatures. Measurements reveal unexpected slippage at $T = 5, 5K$ for a flat surface while for a rough substrate a strict dependance on the external applied load has been found.
Finally I have developed a formula to produce patterned silicon surfaces via micro contact printing of alkylsilane. Preliminary tribological studies have been done with a modified AFM tip having a square tip with a contact area of $\sim 2 \times 2 \mu m^2$. Measurements reveal a reduction of the friction coefficient for OTS patterned surface by a factor 2 with respect to bare silicon.
Introduction

Tribology is the science and technology of interacting surfaces in relative motion[1]. It includes the study and application of the principles of friction, lubrication and wear. The word tribology is based upon the Greek tribos meaning ‘to rub’. Since surface interactions dictate or control the functioning of practically every device developed by man, tribology has been of central importance for thousands of years. The first practical aspects of friction have their roots in prehistory and along all the human history different strategies were studied to reduce friction and wear. For example Egyptian used wooden rollers to move blocks of stone or statues and liquid lubricant to slide blocks accurately into place. Romans reduced the wear of their soles driving nails in the leather[2]. The first recorded systematic study in the field of tribology is due to Leonardo da Vinci, who in his Codex disclosed the first two laws of friction usually attributed to Amontons[3]. The very comprehensive study on the sliding friction was done two hundreds years later by Coulomb that systematically studied the influence of the five main factors upon friction (nature of materials, extent of surface area, normal force, length of time the surfaces remained in stationary contact and ambient conditions). Thanks to many experimental data, he constructed empirical relations, in particular $F = \mu L$ ($L$ is the normal load), finding that $\mu$ doesn’t depend on $L$, on sliding velocity and on contact area. The correct explanation of the empirical relation found by Coulomb was done in the first decades of the 20th century by Tabor and Bowden[4], in terms of the crucial difference between apparent and real area of contact due to the surface roughness.

A new impulse in friction studies was done in very recent years by the design and development of miniaturized systems for which reduced dimensions mean an increase in the friction influence because of the increase of the surface to volume ratio. Micro-Electro-Mechanical Systems (MEMS) are the most developed and used in commercial products like cellulars, automotive sensors, joysticks and so on. A MEMS is the integration of mechanical elements, sensors, actuators and electronics on a common silicon substrate through microfabrication technology. Figure 1 shows some examples of realized MEMS. The reduced dimensions do not allow to use liquid lubricant. Dry lubricants could be a right answer for the problem. Nevertheless, the understanding of microscopically mechanisms involved in friction and wear processes is necessary to improve the life time and performances of these systems.
Figure 1: Examples of MEMS.

One possibility is to change the chemical properties of the surface by using a suitable Self Assembled Monolayers (SAM). Recent studies showed that the friction coefficient of alkylthiol SAM is lower than that of gold[42]. The same behavior is shown by alkylsilane SAM on silicon[5] surfaces.

Let us consider the most simple system formed by a flat substrate with some adsorbed atoms (adatoms). If the substrate is a metal two mechanisms are involved in the friction process: the first one consists in the excitation of phonons in the substrate, while the other one is relative to the drag of electrons due to their coupling with the moving adsorbate. The electronic channel for dissipation can be eliminated working in the superconducting state. If this were confirmed, this would mean that one can reduce friction by freezing the electronic channel for dissipation in a metal.

Another strategy, suggested by recent studies carried out by Dienwiebel et al.[6], consists in using incommensurate surfaces in contact to reduce friction because the sliding friction between two surfaces is very low when they are incommensurated.

Since late 80’s new powerful experimental techniques, such as Atomic Force Microscope (AFM), Surface Force Apparatus (SFA) and Quartz Crystal Microbalance (QCM) have succesfully been applied to the study of sliding friction. Despite numerous studies on the microscopic processes of dry friction, fundamental questions are still unanswered. For instance, in the case of a solid monolayer adsorbed on a flat surface does the sliding friction become larger if the substrate is a metal rather than an insulator? An answer to such a question can be provided by studies of the sliding friction on a superconductor: the observation of a change in friction at the superconducting transition temperature of the substrate, $T_c$, can only be ascribed to the freezing of the electronic dissipation channel. Another question is: two incommensurated solids experience always a low friction regime? And also: is the SAM coating a versatile strategy in the reduction of friction in MEMS?

In this thesis work I have studied the microscopic friction mechanisms. First of all, with the QCM technique I have investigated the electronic contribution to dissipation studying friction of nitrogen and rare gases adsorbed films on a lead sur-
face crossing the superconducting transition. Another way to evaluate the electronic contribution is to cover the metallic surface with an insulating layer to reduce the coupling between surface electrons and adatoms. Then, I have studied the friction variation of Neon adsorbed on gold with increasing Krypton overlayers.

The influence of the surfaces structure has also been studied with QCM technique for gold nanoparticles deposited on a gold surface and for Ne film adsorbed on lead surfaces.

Finally, I have developed a formula to produce patterned silicon surface via micro contact printing of alkyl silane. The tribological properties of the produced samples have been studied with the AFM.

This thesis is organized as follows: the first chapter gives a brief overview of the theoretical models describing the studied systems; in the second chapter the UHV apparatus for QCM measurement is shown; the third chapter gives an overview of the soft lithographic technique involved in the microstructured silicon samples; the fourth chapter illustrates experimental results for friction QCM measurements and finally the fifth chapter shows the preparation of patterned silicon surfaces and the experimental measurements of friction on these samples taken with a modified AFM tip.