

1.1 Surface diffusion

(a) Using linear optical diffraction technique

Surface diffusion is one of the many surface processes which are both fundamentally and technologically important. It plays vital roles in crystal growth, thin film epitaxy, surface chemical reaction, surface catalysis, and corrosion. The previously available techniques suffer different problems such as specific to particular systems (FIM, FEM), too small dynamic range, or complicated and indirect relations for diffusion coefficient extraction. We have successfully developed a linear optical diffraction technique for surface diffusion study [1]. Compared to other techniques, this optical technique has a number of advantages: i) it involves a one dimensional diffusion process and the diffusion coefficient can be easily extracted; ii) it can measure a wide dynamic range of diffusion coefficient, as much as 9 orders of magnitude, from 10^{-6} to 10^{-15} cm^2/sec , while others can only measure ~ 3 orders of magnitude or less; iii) it can readily measure anisotropic diffusion; iv) there is no limitation on the substrates, either metals, or semiconductors, or insulators are all possible; v) it has a very high sensitivity so that the coverage dependence of diffusion can be investigated.

With this technique, over the years, we have systematically studied a wide range of effects such as coverage [2-5], anisotropy [6,7], impurity [8-10], step [4,5,11-14], and phase transition [13,14] on diffusion for gas atom or molecules on a number of metal substrates. The conclusions obtained not only enrich our fundamental understandings on the diffusion process itself but also shed light in surface chemical reaction and catalysis in particular, and thin film epitaxy and crystal growth in general.

For CO/Ni(110) [2], CO/Pt(111) [3], H/W(100) [4], and H/Pt(111) [5], the coverage effect has been fully studied. Since we can make a shallow coverage grating, i.e., with a small coverage difference ($\sim 0.02\text{ML}$) between the high and low surface density regions, the interactions among the molecules are easily extracted out, either within mean field approximation or the quasi-chemical approximation. For the above systems, the adsorbate-adsorbate interactions were found dominantly repulsive and speed up diffusion as coverage increases.

For diffusion over a length scale of microns, steps are often a concern and their effects on diffusion must be studied. We have systematically studied step effect for CO/Pt(111) [11,12,13], H/W(100) [4], H/Pt(111) [5] with controlled step densities via miscutting the surface with different amount. These three systems actually represent different step effects: While for CO/Pt(111), the normal step hindrance of diffusion was observed, diffusion of H/W(100) was found to be little affected by steps. On the other hand, for H on Pt(111) it was found that diffusion actually speeds up on stepped surfaces, in strong contrast to the conventional picture of step effect, calling for a non-local mechanism to explain the results.

It is particularly worthwhile to study CO diffusion on Pt(111). Surprisingly, six groups in the last thirty years have measured the surface diffusion coefficient of this system by a variety of techniques. Yet, the results, both the diffusion activation energy and prefactor, were scattered at significant discrepancies. We have taken the optical diffraction method to examine the problem. Working on well characterized stepped Pt(111) surfaces, we have discovered that the step effect can explain most of the discrepancies observed in the past [3]. In addition, we observed a number of interesting phenomena for CO diffusion perpendicular and parallel to the steps, such as very different prefactors on terraces, across steps, and parallel to steps; a new step-parallel diffusion channel that strongly dependent on step orientations [10,12-14].

We have also studied impurity [8-10] and phase transition [4,15] effect on surface diffusion. In the case of S on Ni(110) [8,9], we found that a low degree of impurity contamination of $\sim 1\%$ ML of S could already affect CO diffusion dramatically, an unexpected results. The observation is important not only for re-interpretation of many previous measurements but also for theoretical understanding of the diffusion mechanism over areas larger than a terrace width. We have developed a model to explain our observation. Phase transition has been predicted to affect surface diffusion for a long time. However, clear experimental demonstration is rare. For H on W(100) [4,15], we have shown that a second order phase transition of the substrate clearly slows down surface diffusion, verifying the theory and moreover supplement the theory with important finite size effect.

(b) Using scanning tunnelling microscopy

Recently, we have developed a new operation mode with scanning tunnelling microscopy to measure diffusion within a nano-region confined by surface potential heterogeneity. Compared to previous STM modes for diffusion measurement, our method can measure at least 4 orders of magnitude faster diffusion and provides

information on the site specific hopping rate. With this method, one may detect quantum diffusion of H ($\sim 10^{-12}$ cm²/sec) which was inaccessible with STM before. The inaccessibility to fast diffusion measurement by STM is an obstacle in the past for its application to a wide range of practically important systems. We have used this method to measure diffusion of a number of metallic atoms confined in the half unit cell of Si(111)7x7 [16].

Publications:

1. Xu-dong Xiao, Yuanlin Xie, and Y. R. Shen, "Surface Diffusion Probed by Linear Optical Diffraction", Surf. Sci. **271**, 295-298(1992).
2. Xu-dong Xiao, Yuanlin Xie, and Y. R. Shen, "Coverage Dependent Surface Diffusion Study of An Anisotropic System: CO/Ni(110)", Phys. Rev. B. **48**, 17 452-17 462(1993).
3. Jianwei Ma, Xudong Xiao, N. J. DiNardo, and M. M. T. Loy, "Diffusion of CO on Pt(111) studied by optical diffraction method", Phys. Rev. B **58**, 4977-4983(1998).
4. Lei Cai, Chaozhi Zheng, K.L. Man, M.S. Altman, E. Granato, T. Ala-Nissila, S. C. Ying, Xudong Xiao, "Step effects on diffusion near a substrate reconstructive phase transition: H on W(100)", Phys. Rev. B **68**, 075422 (2003).
5. C. Z. Zheng, C. K. Yeung, M. M. T. Loy, Xudong Xiao, "Step effects and coverage dependence of hydrogen atom diffusion on Pt (111) surfaces", Phys. Rev. B **70**, 205402 (2004).
6. Xu-dong Xiao, X. D. Zhu, W. Daum, and Y. R. Shen, "Anisotropic Surface Diffusion of CO on Ni(110)", Phys. Rev. Lett. **66**, 2352-2355(1991).
7. Xu-dong Xiao, X. D. Zhu, W. Daum, and Y. R. Shen, "Optical Second Harmonic Diffraction Study of Anisotropic Surface Diffusion: CO on Ni(110)", Phys. Rev. B **46**, 9732-9743(1992).
8. Xu-dong Xiao, Yuanlin Xie, Christian Jacobsen, Heather Galloway, Miquel Salmeron, and Y. R. Shen, "Impurity Effect on Surface Diffusion: CO/S/Ni(110)", Phys. Rev. Lett. **74**, 3860-3863(1995).
9. Xudong Xiao, Yuanlin Xie, Christian Jakobsen and Y. R. Shen, "Effects of surface impurities on surface diffusion of CO on Ni(110)", Phys. Rev. B **56**, 12,529-12,538(1997).
10. Jianwei Ma, Xudong Xiao, and M. M. T. Loy, "Observation of two diffusion channels in a single diffusion measurement: CO on P-contaminated Pt(111) surface", Surf. Sci. **423**, 85-89(1999).
11. Jianwei Ma, Lei Cai, Xudong Xiao and M. M. T. Loy, "On the mechanism limiting CO diffusion perpendicular to steps on Pt(111)", Surf. Sci. **425**, 131-137(1999).
12. Jianwei Ma, Xudong Xiao, and M. M. T. Loy, "Experimental study of surface diffusion rate enhancement along steps: CO on Pt(111)", Surf. Sci. **436**, L661-665(1999).
13. Xudong Xiao, "Step effects on surface diffusion: a comprehensive study of CO on Pt(111)", pp117-127, NATO Science Series, Collective diffusion on surfaces: Correlation effects and adatom interactions, Ed. M. C. Tringides and Z. Chvoj, 2001 Kluwer Academic Publishers.
14. X. R. Wang, Xudong Xiao, and Z. Y. Zhang, "Apparent anomalous prefactor enhancement for surface diffusion due to surface defects", Surf. Sci. **512**, L361-366(2002).
15. Lei Cai, M. S. Altman, E. Granato, T. Ala-Nissila, S. C. Ying, Xudong Xiao, "Surface Diffusion Anomaly Near Substrate Phase Transition: H on W(100)", Phys. Rev. Lett. **88**, 226105(2002).

16. Kedong Wang, Chun Zhang, M. M. T. Loy, and Xudong Xiao, “Time dependent tunneling spectroscopy for studying surface diffusion confined in nanostructures”, Phys. Rev. Lett. in press.

1.2 Nanotribology study using atomic force microscopy

Tribology, a study of friction, adhesion, and wear, is an old subject of science. However, tribology study at nanometer scales, nanotribology, has become a focused study in recent years not only because of the search for fundamental understanding of the origin of friction, adhesion, and wear, and the application in magnetic data storage systems and in micro-electro-mechanical systems, but more importantly because of the invention of atomic force microscope (AFM), which made the study of tribology at this scale possible. In the age of reduced device size in both electronics and micromachines, understanding and control of tribological properties at nanometer scales is increasingly important.

We are among the first to study tribology using AFM, and its offspring frictional force microscopy (FFM), in particular for quantitative measurements. Our measurement on mica [1] represented the beginning of quantitative nanotribology. Our work on lubricant monolayer [2-5] also stimulated continuous interest on the subject.

In quantitative nanotribology measurement, we first carefully characterized the properties of clean mica surface and established it as a reference [1]. This reduces or even eliminates the uncertainties involved in AFM cantilever force constants, tip chemistry, and tip size and shape. With the later development to quantitatively measure the normal and lateral force constants for AFM cantilevers, quantitative nanotribology on any sample becomes possible and comparison between results among different groups becomes meaningful. Our study on the chain length dependence of lubrication effect of alkylsilane monolayers on mica is also a representative work in such a direction [5].

During recent years in HKUST, we have been focusing on two topics of nanotribology: (1) to identify energy dissipation channels in frictional process at nano scale; and (2) to study environment effects on organic monolayer lubricants. For the former, we wanted to control the degrees of freedom of motion and isolate one that can be controlled for energy dissipation study. For example, C_{60} single crystal undergoes an orientational order-disorder phase transition, in which the molecular rotational degree of freedom changes from a free one to a hindered one. Measurement of frictional and adhesion properties across the phase transition allow us to conclude that this degree of freedom only affects adhesion but does not provide effective energy dissipation mechanism [6]. In an alkanethiol monolayer film, the packing structure can be changed via thermal treatment. We found that for compact packing the friction is small but for open packing the friction drastically increases [7,8]. This phenomenon can be explained by that the creation of gauche defects in the open structure would dissipate energy. These fundamental studies enriched our understanding to the origin of friction in particular from the fundamental excitation point of view.

The environmental effect on monolayer lubricants is important in their applications. Here, we have to characterize the binding strength between the monolayer to the substrate and among the monolayer itself [9]. We have further studied how humidity and temperature affect their lubrication performance. We found that the alkylsilane lubricants can help reduce the stiction of Si/Si contact significantly [9-14]. In addition, the reduction of the adhesion is only weakly humidity dependent. For alkanethiol on Au(111), we found that the monolayer can have different structures, which in turn results in different friction. Those results are keen for their applications in magnetic storage and micromachine systems since durability and environmental change are the factors that must be considered.

Recently, we expanded our direction to study glass-to-rubber phase transition of polymers by using the adhesion and friction measurements [15-18]. Such studies provide important information on the behavior of polymer surfaces in contrast with polymer bulk.

Publications:

1. Jun Hu, Xu-dong Xiao, D. Frank Ogletree, and M. Salmeron, “ Atomic scale friction and wear of mica”, Surf. Sci. **327**, 358-370(1995).

2. Xu-dong Xiao, Gang-yu Liu, Deborah H. Charych and Miquel Salmeron, "Preparation, structure and mechanical stability of alkylsilane monolayers on mica", *Langmuir* **11**, 1600-1604(1995).
3. Quan Du, Xu-dong Xiao, Deborah H. Charych, F. Wolf, P. Franz, D. Frank Ogletree, Y. R. Shen and Miquel Salmeron, " Nonlinear optical study of monomolecular films under pressure", *Phys. Rev. B* **51**, 7456-7463(1995).
4. D. Frank Ogletree, Jun Hu, Xu-dong Xiao, Carmen Morant, Qing Dai, Rudiger Vollmer, Robert Carpick and Miquel Salmeron, " Friction and load on well defined surfaces studied by atomic force microscopy", **pp337-344**, *Forces in scanning probe methods*, eds. H.-J. Guntherodt, D. Anselmetti and E. Meyer, NATO ASI series E: Applied Sciences. 1995 Kluwer Academic Publishers, the Netherlands.
5. Xu-dong Xiao, Jun Hu, Deborah H. Charych and Miquel Salmeron, "Chain length dependence of the frictional properties of alkylsilane molecules self-assembled on mica studied by atomic force microscopy", *Langmuir* **12**, 235-237(1996).
6. Qi Liang, O. K. C. Tsui, Yabo Xu, Hongnian Li, Xudong Xiao, "Effect of C₆₀ Molecular Rotation on Nanotribology", *Phys. Rev. Lett.* **90**, 146102 (2003). Selected for publication in *Virtual Journal of Nanoscale Science & Technology*, vol. 7, issue 16 (2003).
7. Xudong Xiao, Bing Wang, Chun Zhang, Z. Yang, M. M. T. Loy, "Thermal annealing effect of alkanethiol monolayers on Au(111) in air", *Surf. Sci.* **472**,41-50(2001).
8. Chun Zhang, Qi Liang, Bing Wang, and Xudong Xiao, "Frictional properties of alkanethiol self-assembled monolayers with different thermal annealing", *J. Appl. Phys.* **95**, 3411-3416(2004). Selected for publication in *Virtual Journal of Nanoscale Science & Technology*, vol. 9, issue 12 (2004).
9. Fang Tian, Xudong Xiao, M. M. T. Loy, Chen Wang, and Chunli Bai, " Humidity and temperature effect on frictional properties of mica and alkylsilane monolayer self-assembled on mica", *Langmuir* **15**, 244-249(1999).
10. Xudong Xiao, Chun Zhang, Bing Wang, "Tribological properties of self-assembled monolayers", **pp184-187**, *Physics and chemistry of nanostructured materials*, eds. Shihe Yang and Ping Sheng, 2000 Taylor & Francis, London.
11. Linmao Qian, Xudong Xiao, Shizhu Wen, "Tip in-situ chemical modification and its effects on tribological measurements", *Langmuir* **16**, 662-670(2000).
12. Xudong Xiao, Linmao Qian, "Investigation of Humidity Dependent Capillary Force", *Langmuir* **16**, 8153-8158(2000).
13. Linmao Qian, Fang Tian, Xudong Xiao, "Tribological properties of self-assembled monolayers and their substrates under various humid environments", *Tribology Letters* **15**, 169-176 (2003).
14. Sili Ren, Shengrong Yang, Yapu Zhao, Tongxi Yu, Xudong Xiao, "Preparation and Characterization of an Ultrahydrophobic Surface Based on a Stearic Acid Self-Assembled Monolayer over Polyethyleneimine Thin Films", *Surf. Sci.* **546**, 64-74(2003).
15. O. K. C. Tsui, X. P. Wang, Jacob Y. L. Ho, T. K. Ng, Xudong Xiao, "Studying surface galss-to-rubber transition using atomic force microscopic adhesion measurements", *Macromolecules* **33**, 4198-4204(2000).
16. X. P. Wang, Xudong Xiao, O. K. C. Tsui, "Surface Viscoelasticity Studies of Ultrathin Polymer Films Using Atomic Force Microscopic Adhesion Measurements", *Macromolecules* **34**, 4180-4185 (2001).

17.X. P. Wang, M. M. T. Loy, Xudong Xiao, “Bundle Structure Formation on a Polymer Film at Various Temperature and AFM Scanning Velocity”, *Nanotechnology* 13(4), 478-483 (2002).

18.X. P. Wang, O. K. C. Tsui, Xudong Xiao, “Dynamic Study of Polymer Films by Friction Force Microscopy With Continuously Varying Load”, *Langmuir* 18, 7066-7072(2002).

1.3 Novel properties of nano structures and nanomaterials

Nano science is an active research field in recent years. We are making use of the optical and microscopic tools to actively study the properties of nanostructures and nanomaterials.

Metal clusters of nanometer sizes are interesting because they often exhibit novel physical and chemical properties. Due to the small size, when placed in a double-barrier tunnel-junction (DBTJ) geometry, discrete charging properties such as Coulomb blockade and Coulomb staircases show up. When the size of the cluster is small enough, the energy levels may become discrete as well due to quantum size effect. Again, the quantized energy levels can be observed in the tunnelling spectroscopy. The discrete charging effect can be used to realize single electron transistor devices, a base for future generation electronics. In the past years, we have studied Au clusters evaporated on alkylthiol/Au(111) [1,2,3]. The Au clusters are of two dimensional. It is found that the Coulomb blockade/Coulomb staircases still exists, with some detail difference from the three dimensional clusters [4]. Because of the two dimensionality, the size of the clusters can be measured by STM precisely while the tunneling spectrum is being taken. With the size information, we can check the validity of the theory directly. By reducing the distance between an STM tip and the cluster, we have found some intriguing tunneling behaviour [3]: *The width of the Coulomb blockade ($e/2C$) first decreases as a consequence of increased capacitance, and then increases due to “quantum capacitance” of the junction.* Our observation established the quantum effect of capacitance for the first time by experiment.

Carbon nanotube is another topic that attracts intensive research in the last decade. It is regarded as a key materials in nano-technology. While single-walled carbon nanotubes are known to exhibit many interesting mechanical and electrical properties due to their unique one-dimensional (1D) structures, only recently photoluminescence (PL) from the direct band gap semiconducting carbon nanotubes was reported, which may extend the possible applications to optoelectronics. We found that strong visible PL was emitted from metallic (3,3) tubes and from indirect narrow band-gap (~ 0.2 eV) semiconducting (4,2) tubes, which become metallic after N-doping [5]. Compared to bulk gold and copper which have a PL efficiency of only $\sim 10^{-10}$, our discovery demonstrates that 1D metals could be much more efficient PL emitters.

Publications:

1. Bing Wang, Xudong Xiao, Ping Sheng, “Growth and characterization of Au clusters on alkanethiol self-assembled monolayers”, *J. Vac. Sci. Technol. B* **18**,2351-2358(2000).
2. Bing Wang, Xudong Xiao, Xianxiang Huang, J. G. Hou, Ping Sheng, “Single-electron tunneling study of two-dimensional gold clusters”, *Appl. Phys. Lett.* **77**, 1179-1181(2000).
3. J. G. Hou, Bing Wang, Jinlong Yang, X. R. Wang, H. Q. Wang, Qingshi Zhu, and Xudong Xiao, “Nonclassical behavior in the capacitance of a nanojunction”, *Phys. Rev. Lett.* **86**, 5321-5324(2001).
4. Bing Wang, Haiqian Wang, Huixiang Li, Changgan Zeng, J. G. Hou, Xudong Xiao, “Tunable single-electron tunnelling behavior of ligand-stabilized gold particles on self-assembled monolayers”, *Phys. Rev. B* **63**, 035403-(1-7) (2001).
5. Jiandong Guo, Chunlei Yang, Z. M. Li, Ming Bai, H. J. Liu, G. D. Li, E. G. Wang, C. T. Chan, Z. K. Tang, W. K. Ge, and Xudong Xiao, “Efficient Visible Photoluminescence from Carbon Nanotubes in Zeolite Templates”, *Phys. Rev. Lett.* **93**, 017402(2004). Selected for publication in *Virtual Journal of Nanoscale Science & Technology*, vol. 10, issue 2 (2004).