Nano-scale tribology study of organic adlayer-metal interface using quartz crystal microbalance combined with scanning tunneling microscopy

Sang M. Lee, M. Abdelmaksoud* and J. Krim
Physics Department, Box 8202, North Carolina State University, Raleigh, North Carolina, 27695-8202, USA
*Physics Department, Cairo University, Giza, Egypt

ABSTRACT
A quartz crystal microbalance combined with scanning tunneling microscopy (STM-QCM) was used to investigate the interactions between organic adlayers ($C_6H_6$ and $C_6H_5I$) on Cu surfaces and a metallic STM tip. STM images of $C_6H_6$ covered Cu surface improved when the QCM was simultaneously oscillated during the imaging. In contrast, STM images of $C_6H_5I$ covered surfaces became noisy when the sample was oscillated. The two systems moreover exhibited frequency changes of opposite signs in response to STM tip contact, indicative of different physical phenomena at the surface. The dependence of the STM image quality and the frequency shift were interpreted in terms of the adsorbate-substrate chemical and physical interactions, and different levels of frictional heating at the interface.

INTRODUCTION
The understanding of nano-scale tribology has emerged as an important area in micro-electro mechanical system (MEMS) and nano-electro mechanical system (NEMS) engineering to improve device function. The sharp resonance of a quartz crystal microbalance (QCM) is sensitive to interaction forces applied to its surfaces, and the QCM has been employed to obtain the fundamental information on energy dissipation mechanisms associated with the sliding of atomically thin films along surfaces. In this study a QCM was combined with scanning tunneling microscopy (STM) to investigate the interactions between organic adlayers and metallic STM tip. While STM allows the direct imaging of films adsorbed on the QCM electrode under both stationary and oscillating conditions and the nanotribological behavior of copper surfaces covered by $C_6H_6$ and $C_6H_5I$ was studied by means of QCM-STM. During the STM tip indentation, the change in resonance frequency of the QCM was monitored to explore the response of the each organic layer covered QCM to the mechanical perturbation. The direction of the frequency shift in the QCM-probe interaction [1,2] is likely to indicate whether the interface is solid or liquidlike in nature. We observed the shifts in both directions depending on the organic adlayers. The result is of great relevance to MEMS and NEMS devices, where melting of a sliding contact can damage or destroy the device.

Experiments

Figure 1. A schematic diagram of the experimental system. The STM tip scans the surface of a vibrating quartz disk, at its center, to measure the change in oscillation frequency and amplitude of the fundamental transverse shear mode. All works were done in-situ under ultrahigh vacuum environment.

Our experimental arrangement is shown schematically in Figure 1. The QCM oscillators employed for this study were 8 MHz fundamental mode “AT-cut” (transverse-shear mode) crystals identical to those which are routinely employed as QCM. To start from clean surface, the additional 1000 Å of Cu was deposited on the electrode of QCM by thermal evaporation at the pressure of $1 \times 10^{-8}$ Torr. The organic molecules were dosed by back-filling the chamber with their vapors, $1 \times 10^{-3}$ Torr for $C_6H_6$ and $1 \times 10^{-5}$ Torr for $C_6H_5I$. 
During imaging, the QCM was turned on and off to see the effect of the oscillation to the quality of STM images. For the STM tip indentation, the frequency shift of QCM was monitored to investigate its effects to the tip-surface interaction.

RESULTS AND DISCUSSION

Figure 2. The change of image quality with QCM oscillation during imaging. (a) C₆H₆ on Cu – The initially noisy image quality was improved its quality with the coupling of the oscillation. (b) C₆H₅I on Cu – The initially clear image quality was degraded with the coupling of the oscillation.

The response of both surfaces to the STM scanning, the STM scanning coupled with QCM oscillation, and the change of oscillation frequency with STM-tip indentation were different each other. When the QCM was turned off, the scanned image of C₆H₆ on Cu was noisy while that of C₆H₅I on Cu surface was clear. This image quality difference immediately inverted when the QCM oscillation was coupled with scanning. (Figure 2) This observation implies that the interaction of these molecular layers with STM tip are very different each other. Since the STM imaging reads the electronic structure of a surface, we can infer that the poor conductivity of C₆H₆ on Cu surface was significantly improved by the coupling of QCM oscillation. However, the relatively good conductivity becomes worse with the oscillation for the case of C₆H₅I on Cu surface.

When a STM-tip was indented during QCM oscillation, the frequency shift for the C₆H₆ on Cu surface was positive while the shift for the C₆H₅I on Cu surface was negative. (Figure 3) This may indicate the modes of the adlayers’ existence on Cu surface are different. According to Borovsky and Krim’s model, the frequency shift is towards positive with solid surface and towards negative with liquid surface.[3] However further investigation should be performed from both theoretical and experimental aspects for the better understanding of this observation.

CONCLUSION

The different response of organic adlayers (C₆H₆ and C₆H₅I on Cu surface) to the STM scanning, the scanning coupled with the sample oscillation, and the STM-tip indentation was observed, and discussed in terms of surface conductivity and the mode of adlayer’s existence on Cu surface.

Figure 3. The frequency shift of QCM with the STM-tip indentation. (a) C₆H₆ on Cu surface – The frequency shift was towards positive direction and becomes saturated with indentation depth. (b) C₆H₅I on Cu surface – The frequency shift was towards negative direction and about 100 times larger than that of C₆H₆ on Cu surface case.

ACKNOWLEDGMENTS

This work has been supported by DOE #DE-FG02-01ER4593

REFERENCES