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KEY ROLE OF M.G. NAKHODKIN'S INSIGHT AND INSPIRATION IN DEVELOPMENT OF UHV STM-RELATED TECHNIQUES AND METHODS

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I briefly describe my joint efforts and experiences with M.G. Nakhodkin in the field of scanning tunneling microscopy (STM), including a construction of home-built microscopes, the application of this technique in various scientific endeavours, fruitful and enlightening discussions, and the collaboration on the international scale with M.G. Nakhodkin and members of his scientific group. Our co-operation was focused on the novel aspects of the preparation and the conditioning of STM probes, coupling the STM junction with laser irradiation, and STM-based nanolithography.

K e y w o r d s: surface, scanning tunneling microscopy.

1. Introduction

Before coming to the United States in 1996 as a visiting scientist at the University of Pittsburgh, I had worked as a senior member of the technical staff at the Faculty of Radiophysics of the Taras Shevchenko National University of Kiev since 1989. While there, I worked under the indispensable guidance of Mykola Grygorovych Nakhodkin and received, from him and other colleagues, the invaluable scientific and technical help in my research activities. From the very beginning, Nakhodkin strongly supported the idea of the rapid development of scanning tunneling microscopy/spectroscopy (STM/S) methods for surface science studies.

Using my previous experience garnered at the Leningrad State University with an air STM, built there first in the Soviet Union (1986), Nakhodkin suggested extending this method for the evaluation of the sample surface roughness in Elastic Electron Reflection Spectroscopy. As a result, one of the first papers in the Ukraine, where the STM technique was used, was published in 1990 [1]. One year later, the air STM also was used in studying the thin film surface morphology in the nanometer range [2]. However, one of the greatest achievements at the Faculty of Radiophysics during that time was the design, development, assembling, and testing of an ultrahigh vacuum (UHV) STM, the first built in the Ukraine (1992). This project benefited tremendously from Nakhodkin's generous and continuous support. The unique compact design of the instrument [3] has allowed its straightforward and reliable incorporation into practically any UHV system [4]. Furthermore, it has permitted an *in situ* combination of the STM with other surface analysis techniques, including, for example, Auger Electron Spectroscopy (AES) [5].

As a senior research scientist at the Pacific Northwest National Laboratory (PNNL) since 2002, I still specialize in the application area of UHV STM/S methods to surface science studies, basically following a scientific pathway foreseen by my close and fruitful cooperation with Nakhodkin. Currently, I am applying STM for studying the surface chemistry of metal oxide materials at the atomic level. My research includes the investigation of the physical and chemical processes governing the thermal- and photoinduced reactivity of adsorbed molecules with the use, in addition to the scanning probe techniques, of other surface analysis methods such as AES, X-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED).

As part of my entry in this collection of articles, I have included a few examples that clearly illustrate how Nakhodkin's long-term encouragement, advice, and foresight continue to play a crucial part in developing my scientific career in the U.S.

2. Experimental

My work on the reproducible tip fabrication and cleaning for UHV STM started at the Faculty of Ra-

diophysics back in Kiev and since then has further advanced at PNNL. The tip quality is a major factor that determines the performance of the STM. The tip geometry (sharpness), shape (mechanical rigidness), and chemical composition (cleanness) are important for the imaging mechanism and the atomic resolution of the STM. Tips that are used under UHV conditions are frequently made from tungsten because of its high melting temperature, mechanical strength, and simplicity of fabrication using an electrochemical etching process. As a result of the electrochemical etching process (and also the exposure to ambient conditions), the tip is inevitably covered by a residual oxide layer and various contaminants (e.g., etching residuals, hydrocarbons). Hence, for a stable STM operation, the tip should be properly cleaned. While the electrochemical etching mainly controls the tip shape, it is the cleaning process that determines the eventual tip performance. For refractory metals with a relatively high melting point, the annealing of the tip at elevated temperatures in the UHV is a fairly efficient way to remove the surface oxide and contaminants. In addition, the heating will anneal a plastic deformation and other stress-induced defects generated at the tip apex by the electrochemical etching process.

At PNNL, my collaborators and I have developed several technical modifications related to the tip UHV annealing treatment that considerably improve the reliability of the tip preparation for a high-resolution STM [6]. Figure 1, *a* displays the charge coupled device (CCD) camera snapshot showing the actual configuration for the tip annealing by a passing current, displaying both "permanent" and retractable contacts simultaneously touching the tip shank, while the nominal distance between the contacts is of the order of several millimeters. The CCD camera snapshot during the actual tip annealing is presented in Figure 1, *b*, where the tip is held at an elevated temperature of 950 K. Generally, tip temperatures up to 1500 K may be reached reproducibly. In the developed tip annealing setup, the highest temperature region is localized on the tip, as demonstrated in Figure 1, *b*. This allows adjacent components to be less heated, which, in turn, provides the possibility for an accurate tip temperature measurement (by a pyrometer) and causes a considerably less outgassing. To ensure that the tip (and not the contact area) is the hottest spot during the resistive heating,

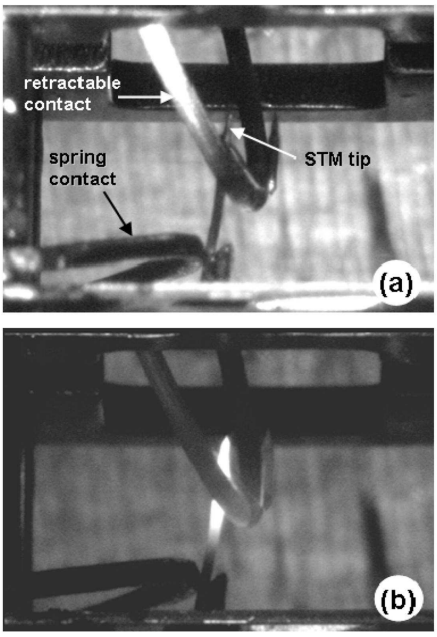


Fig. 1. CCD camera photographs showing (*a*) actual configuration of the developed tip annealing setup; (*b*) the same snapshot during the tip annealing at a temperature of 950 K. (Image (*b*) was acquired with minimal external illumination to take advantage of the CCD camera's near-infrared sensitivity) [6]

a sufficient load has to be applied when making a contact (achieved by a movable contact). There are several other benefits in the presented setup. Placing the tip on the main manipulator of the UHV system in the open configuration offers a possibility for the *in situ* tip characterization with different surface science methods or for the additional cleaning and for sharpening via the ion sputtering. The retractable contact may also be used as a counter electrode for monitoring the tip relative sharpness by a field emission throughout the whole UHV treatment process.

3. Laser-Assisted STM

The studies of a transient tunneling current in laser-assisted STM were inspired by Nakhodkin's original insight on the importance of combining the STM with a laser irradiation *in situ*. When optical irradiation is coupled to the tunneling junction of the STM, a STM response can originate from several sources, including surface photovoltage, thermoelectric potential, opti-

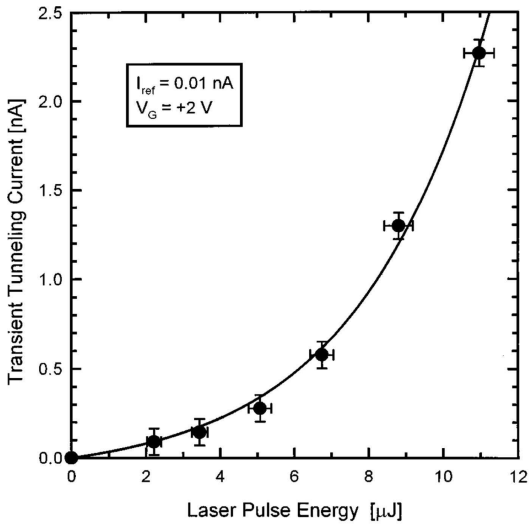


Fig. 2. Dependence of the laser-induced transient tunneling current on the 20-ns laser pulse energy at the constant reference tunneling current, $I_{\rm ref} = 0.01$ nA, and the sample bias voltage $V_{\rm G} = +2$ V. The exponential fit of data is shown as a solid line [8]

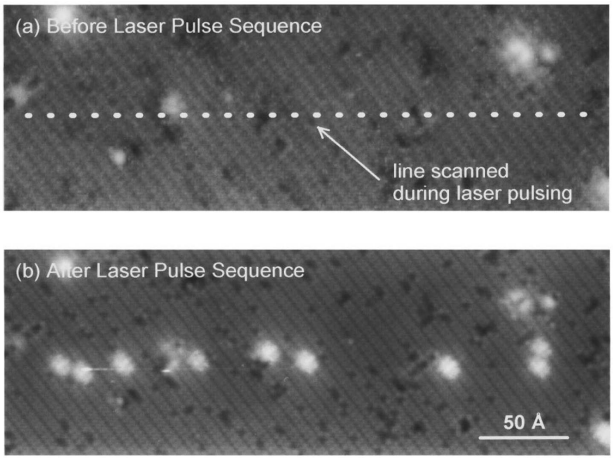
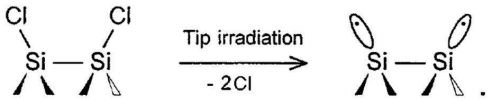


Fig. 3. Empty state topographic images ($V_{\rm G} = +2.5$ V, $I_{\rm ref} = 0.15$ nA) of the same area of the chlorine-saturated Si(100) surface before (a) and after (b) the irradiation (200 laser pulses) of the STM tip in a line scan. The area repeatedly scanned by the STM tip during the laser pulsing is indicated by a dashed line [8]

cal rectification, and thermal expansion, changing the tunneling gap width. Till recently, however, a little attention has been devoted to the induction of the tunneling current by a laser pulse. Different effects, including the thermal expansion of a sample and the tip, Nottingham heating, and hot electron tunneling, have been considered. Studies, which were conducted during my tenure at the University of Pittsburgh, of the transient tunneling current as a function of the laser pulse intensity provide a direct evidence that the transient current is induced by the transient thermal expansion produced by a laser pulse [7, 8]. The dependence of the transient tunneling current on the laser pulse energy is shown in Figure 2, where an exponential increase of the transient tunneling current with an increase of the laser pulse energy is observed. This exponential dependence indicates that the mechanism at work involves the heating and the expansion of the tip in proportion to the laser pulse energy.

Following the path envisioned by Nakhodkin, my PNNL colleagues and I have further used laser pulses for the desorption under the STM tip to achieve a removal of single adsorbed molecules [8]. Since current lithographic techniques used in microelectronic technology are approaching the fundamental limits of their spatial resolution, it is becoming more and more important to find new ways to overcome these limitations. One of the possibilities for creating extremely small structures with dimensions as small as the size of an atom is to use the STM as a tool for perturbing the surface. The strong local interactions achievable between the STM tip and the surface can lead to a selective manipulation of the atoms underneath the tip. Under usual tunneling conditions, the close proximity of the tip does not lead to a local modification of the surface structure. Hence, a standard way to enhance the surface-tip interaction is the reduction of the surface-tip separation or the application of short voltage pulses across the tunneling gap. This leads to an increase of the electrical field and, subsequently, to an increase of the tunneling current, and, possibly, to the local surface heating. All of these factors can lead to the local atom desorption from the surface, to the atom transfer from the surface to the tip, or *vice versa*. A different way to enhance the sample-tip interaction is the irradiation of the STM tip by short laser pulses. Figure 3 demonstrates the local desorption of chlorine atoms from the Si(100) surface site achieved by the laser pulse irradiation of the tunneling gap. We have showed that the observed central bright dimer (which appeared after laser irradiation) represents a bare Si–Si dimer pair after the desorp-

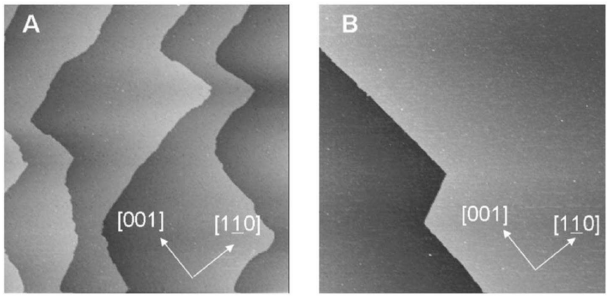
tion of two Cl atoms, as schematically shown in



4. STM Investigations of UHV-Cleaved Samples

As a final example of Nakhodkin's influence on my work, I include the recent results of the STM studies on a $TiO_2(110)$ surface prepared via UHV cleavage [9]. This work was a result of the collaborations with Nakhodkin's former Ph.D. student and later a colleague from the Laboratory of Electron Spectroscopy at the Faculty of Radiophysics, Dr. Oleksandr Bondarchuk (who held the joint appointment at PNNL and the University of Texas at Austin at that time). The $TiO_2(110)$ surface has become a model oxide surface for numerous studies investigating the relationship between the catalytic activity and the surface structure of model oxide catalysts. Under catalytically relevant conditions, the TiO_2 catalyst is usually fully oxidized. In model UHV studies, the sample preparation leads to significantly reduced surfaces with a fraction of missing oxygen atoms. Preparing the stoichiometric TiO_2 surfaces is clearly important in bridging the gap between the model and real catalysts.

TiO_2 crystals of a high quality are commercially available, and the clean (110) surface can be prepared by cycles of ion sputtering and annealing. It usually takes a number of sputtering/annealing cycles (in some cases, more than 10) to prepare the $TiO_2(110)$-(1×1) surface with a contamination level below the detection limit of AES. The total thermal load endured by a sample during the initial cleaning procedure leads to the accumulation of structural defects, such as oxygen vacancies and Ti interstitials. The surface stoichiometry reflects the equilibrium concentration of defects of both types in bulk, and the preparation of a stoichiometric $TiO_2(110)$ surface is a rather challenging task. The clean $TiO_2(110)$-(1×1) surface produced via the *in situ* cleavage of a TiO_2 single crystal has been successfully prepared and imaged with STM. The STM images of a large $(1 \times 1\ \mu m^2)$ area of the $TiO_2(110)$ surfaces prepared via sputter-annealing cycles and on the as-cleaved surface are shown for comparison in Fig. 4. An STM image taken of the as-cleaved sample revealed the surface consisting of extremely wide unreconstructed (1×1) terraces divided by single-height steps with very low kink densities. Correspondingly, Fig. 5 shows an atomically resolved STM image from the as-cleaved $TiO_2(110)$, revealing alternating bright and dark rows running along the ⟨001⟩ direction. The bright rows are spaced along the ⟨1-10⟩ direction with a period of roughly 0.65 nm, which is the periodicity of the rows of Ti^{4+} cations on $TiO_2(110)$-(1×1) surface.



a *b*

Fig. 4. STM images taken on the $TiO_2(110)$ surface prepared by sputtering/annealing (*a*) and by cleavage in UHV (*b*). Scan size: $1 \times 1\ \mu m^2$. (*a*) Bias of 1.52 V, tunneling current of 0.17 nA. (*b*) Bias of 1.2 V, tunneling current of 0.19 nA. Crystal was cleaved after the 20-min annealing at 800 K [9]

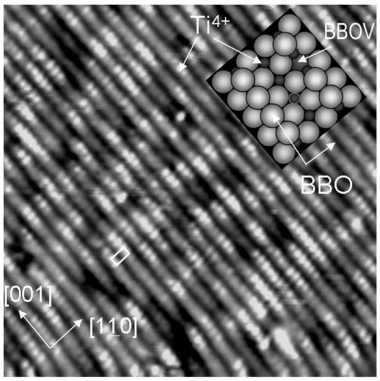


Fig. 5. High-resolution STM image of as-cleaved $TiO_2(110)$. Scan size: $17 \times 17\ nm^2$. Bias of 1.2 V, tunneling current of 0.19 nA. The small white rectangle shows a unit cell of $0.3 \times 0.65\ nm^2$. Inset shows a model $TiO_2(110)$-(1×1) surface with a bridge-bonding oxygen vacancy (BBOV) [9]

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КЛЮЧОВА РОЛЬ ПРОНИКЛИВОСТІ І НАТХНЕННЯ М.Г. НАХОДКІНА У РОЗВИТКУ ТЕХНІКИ І МЕТОДІВ РАСТРОВОЇ ТУНЕЛЬНОЇ МІКРОСКОПІЇ В УМОВАХ НАДВИСОКОГО ВАКУУМУ

Р е з ю м е

Я коротко наводжу нашу спільну з М.Г. Находкіним роботу в області растрової тунельної мікроскопії (РТМ), включаючи створення мікроскопів і застосування цієї техніки в різних наукових завданнях, корисні пояснювальні обговорення, і співпрацю міжнародного масштабу з М.Г. Находкіним і членами його наукової групи. Нашу співпрацю було сфокусовано на нових аспектах виготовлення та досягнення необхідних параметрів РТМ-датчиків; на впливі випромінюванням лазера на область, що досліджується за допомогою РТМ; і нанолітографії на основі РТМ.