Resonance Tunneling of Field Emitted Electrons Through Adsorbates on Metal Surfaces

Initiation of the modern era of surface science, generally acknowledged as starting in the late 1960s, was made possible by two distinct qualitative leaps forward. One was the Sputnik-inspired development of ultra-high vacuum and electron-optical technologies. The other was the recognition and development of theoretical and measurement techniques for studying surface properties and processes on the (single!) atomic level. The field emission spectroscopy result reported in this 1969 NBS paper [1] was the first work in which the electronic energy level spectra of adsorbed atoms was observed and theoretically interpreted. All subsequent electron energy level spectroscopy of adsorbed atoms and molecules, whether based on tunneling processes such as in this work or on photon-induced processes, can legitimately be considered as logical consequences of this pioneering study. The spectroscopic information so obtained is the essential ingredient required in all quantum mechanical modeling of chemical bonding, catalysis, dynamics, and reactivity at solid surfaces, and it is for this reason that the advances reported in this paper have had lasting and historical significance.

The situation at NBS at the time was particularly well suited for the laboratory to become one of the three or four pre-eminent international centers of excellence leading the transformation of then-existing surface studies from a qualitative mystical art into a quantitative and intellectually stimulating hard science in which the basic systems and processes under study could be understood at the most fundamental atomic level. Major efforts in atomic and electron physics were focused on the development of monochromatic electron sources and energy analyzers (of special importance here, the work of John Simpson and Chris Kuyatt) and in their utilization for basic atomic physics studies, particularly those theoretically inspired by Ugo Fano (discussed elsewhere in this volume). A major direction in electron beam production relied upon field emitted/tunneled electrons as a promising source, and it was within this context that Russ Young came to NBS in 1961 and soon was attracting world-wide attention for his measurements and interpretation of field emission energy distributions as a new probe of the electronic state of surfaces [2]. Ward Plummer arrived at NBS in 1967 as an NRC postdoctoral fellow to work with Young. In parallel with this surface work in atomic physics, complementary experimental research within the domain of physical chemistry (also discussed elsewhere in this volume) and in metallurgy (by Al Melmed) gave a cross-disciplinary flavor, across NBS organizational boundaries, to surface science. This situation was successfully used to persuade NBS management to create a new inter-institute position for a surface theorist, which enabled Bill Gadzuk to join NBS in 1968. Almost immediately, it became clear that the intellectual and personal chemistry among Plummer, Gadzuk, and Young was right, and a highly productive collaboration proceeded for the next several years in the area of electron spectroscopy of surfaces, in which all sorts of new things were discovered, studied, and understood. The topic of this paper [1] has perhaps had the most long lasting and global significance, both because it was the first definitive experimental/theoretical study of the quantum states of adsorbates and also because the basic phenomenon of resonance tunneling has been so important in microelectronics and in nanostructures.

The field-emission microscope (FEM) and its derivative spectroscopies are based on the fact that a modest positive potential (~1 keV–3 keV) applied between a sharpened conducting tip (radius ~100 nm) and a flat or concentric spherical electrode, positioned a macroscopic distance (~1 cm–10 cm) away, will result in an electric field at the emitter surface whose strength is ~1 V/nm–10 V/nm, as depicted in Figs. 1 and 2. This field is strong enough to allow electrons to quantum mechanically tunnel from the tip (on the left) into the free space (on the right). Energy analysis of the emitted electrons reveals a total energy distribution (TED) of emitted electrons that is exponentially decreasing in number below the sharp, high energy Fermi edge and which has an ~1.0 eV width under typical field emission conditions [2]. If a fluorescent screen is introduced behind the accelerating electrode, then a spatial distribution of the electron emission from the tip can be imaged. This distribution will have a spatial resolution of a few nanometers. Contrast in the image is due to variations in electron emission across the tip surface, historically attributed to variations in the surface work function. Furthermore, a “small” hole,

called a probe hole, can be made in the screen so that electron emission from a surface region composed of only ~15–30 atoms passes through the hole and then into the energy analyzer. This allows electron spectroscopy studies to be performed on the emission from just these few atoms. Deflection grids are used to focus the emitted current from a chosen portion of the surface over the probe hole. This experimental arrangement is shown in Fig. 1.

When a single atom, molecule, or cluster is adsorbed onto that portion of the surface emitting through the probe hole, if the adsorbate has an electron quasibound state near the Fermi level of the tip, then a substantial increase in the probe-hole current can occur as a result of resonance-tunneling enhancement through the adsorbate. New adsorbate-induced structure in the observed TED reflects the local density of electronic states of the adsorbate, which in turn leads to an unambiguous electron spectroscopy of single adsorbed atoms.

The physical origin of the effect can be understood from the potential energy diagram and wave functions shown in Figure 2. The "triangle barrier" field-emission configuration suggested earlier is here augmented by a potential well whose width $2w$ is roughly the diameter of the adsorbed atom, which is located a distance s from the surface. The electronic state of this atom is characterized by a discrete level which has been broadened into a band, referred to as the local density of states and labeled $\rho_a(\varepsilon)$ in Fig. 2. Enhanced tunneling occurs for those tip states ψ_m whose energy is resonant with $\rho_a(\varepsilon)$, in which case the coherent process of tip-to-atom tunneling constructively interfering with atom-to-free space tunneling occurs with much greater probability (by factors sometimes as large as $\sim 10^2$–10^4) than for direct tip-to-free space tunneling. It is this magnification or amplification that is responsible for the collimated emission from the single adsorbate rising far above the background emission from other parts of the field emitter surface and, as detailed years later [3], is the underlying principle that enables atomic resolution in the scanning tunneling microscope.

In considering the spectroscopic characteristics of emission from the composite surface, it is most informative to measure and display *R,* the ratio of the change in TED to the original TED, as a function of energy. For typical adsorbate conditions, the theory outlined in the initial communication [1] shows that this ratio, for emission from the adsorbate-covered surface area, is

$$R(\varepsilon) \approx \sum_a [\rho_a(\varepsilon)/\rho_m(\varepsilon)]\exp[2\kappa(\varepsilon)(s+w_a)]$$

where the summation includes all the adsorbate states contributing to the tunneling, $\rho_a(\varepsilon)$ is the adsorbate density of states derived from state a, usually represented by a Lorentzian lineshape [4]

$$\rho_a(\varepsilon) \equiv \frac{1}{\pi}\frac{\Delta_a}{(\varepsilon-\varepsilon_a)^2+\Delta_a^2}$$

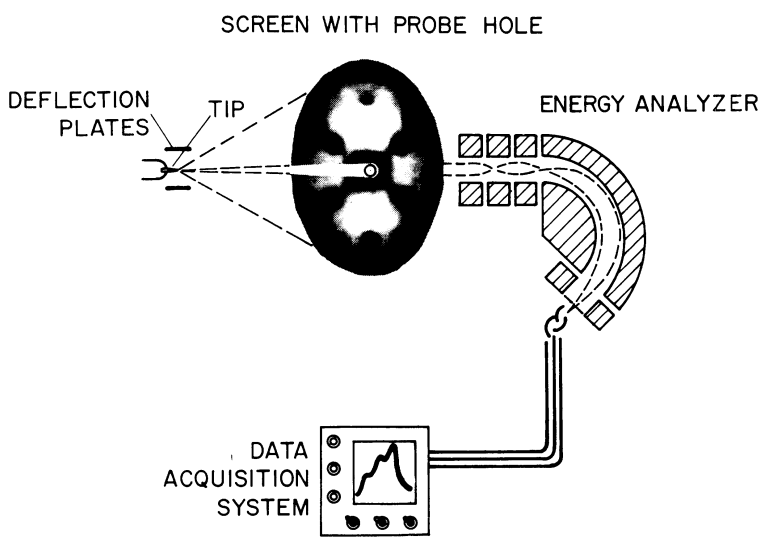

Fig. 1. Schematic drawing of a field emission microscope adapted for energy distribution measurements. The (110) plane of the emitter is positioned over the probe hole. Note that although an electrostatic deflection analyzer is shown here, the data reported in [1] were acquired with a retarding potential analyzer.

with ε_a and Δ_a, the resonance position and width, depending upon the particular state, $\rho_m(\varepsilon)$ the substrate density of states, w_a the "radius" of the atomic state, $\kappa(\varepsilon) \approx [(2m/\hbar)(\phi_e - \varepsilon)]^{1/2}$, and φ_e the workfunction of the tip. Observed structure in the TED that provides the desired spectroscopic information arises from $\rho_a(\varepsilon)$. The enhancement is mainly a consequence of the fact that now the rate-limiting step is tunneling from the adsorbate to vacuum, through a barrier that is reduced compared to the full direct metal-vacuum tunneling barrier. This enhancement is accounted for by the exponential factor. As was noted in the original paper [1], this realization of resonance tunneling involving an adsorbed atom (discrete state mixed with a continuum) can be (and was!) put in one-to-one correspondence with the Fano lineshape theory [4] which is the topic of another NBS/NIST classic publication outlined in this volume.

The initial spectroscopic experiments were carried out for single zirconium atoms deposited on a tungsten field emission tip; the published TED ratio is shown in Figure 3 together with two "relatively good fits" to the theoretical curve. This spectrum, crude even by standards a year later, nonetheless was a landmark. It expressed the first confirmation of the rather speculative beliefs of the time that the electronic energy level spectra of adsorbed atoms were related to the free atom spectra shifted and broadened ~1 eV by interaction with the surface. Refined and extended presentations of this study soon followed which reached a much wider audience [5,6].

An unusually creative and imaginative period of research by the three coauthors over the next few years produced a wealth of new insights into the microscopic aspects of surfaces. The surface topografiner [7] invented and constructed by Young during this time period (and discussed elsewhere in this volume) was an initial version of the scanning tunneling microscope for which the 1986 Nobel Prize in Physics was awarded to Binnig, Rohrer, and Ruska. The field emission spectroscopy work of this period (mostly from NBS) has been summarized and reviewed by Gadzuk and Plummer in their *Reviews of Modern Physics* article [8], which is still one of the most definitive and comprehensive sources of widely used information and wisdom on this topic. The theory of resonance tunneling developed during this period is applicable in many areas of current interest and activity, for instance resonance tunneling in nanostructures such as quantum wells, quantum dots, and in the STM , as discussed in the 1993 *Physical Review* paper by Gadzuk [3].

The members of the trio have followed varied life trajectories over the ensuing decades. In 1973 Plummer joined the faculty at University of Pennsylvania, where he served as director of the Materials Research Laboratory from 1990 to 1992. Since 1992 he has held a joint

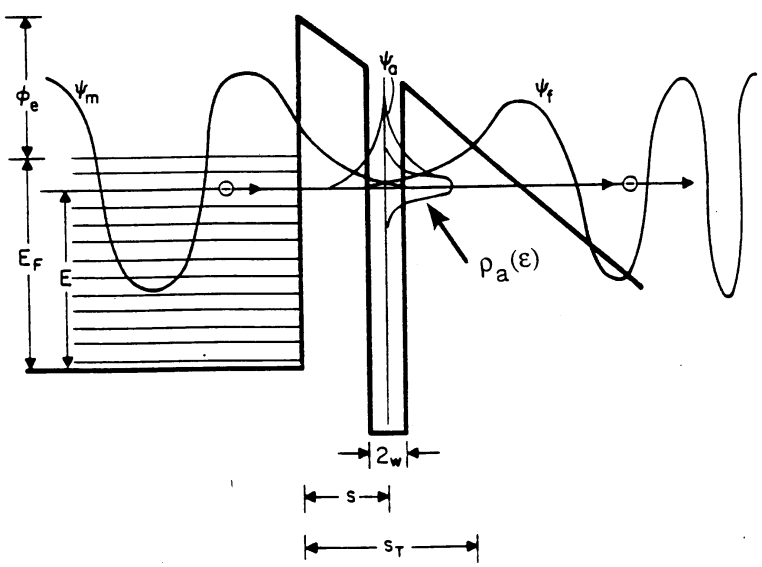

Fig. 2. Schematic model showing the idealized potentials relevant in field-emission resonance tunneling. The electron wave functions are: ψ_m, the unperturbed metal function; ψ_a, the localized adsorbate resonance function; and ψ_f, the emitted electron function. The adatom centered at $z = s$, with diameter equal to $2w$, shows a Lorentzian-like local density of states labeled ρ_a.

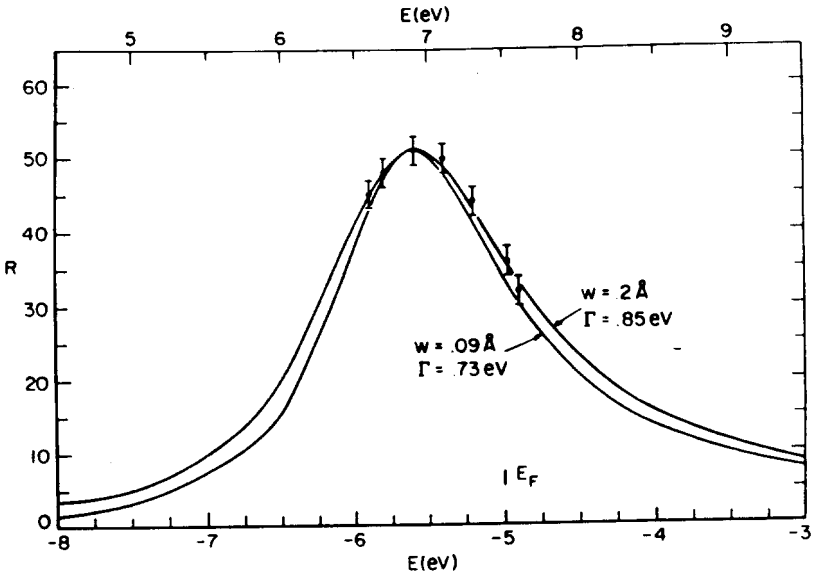

Fig. 3. Energy dependence of the ratio of the adsorbate-induced change in the TED to that of the clean surface, $R \equiv \Delta j'(\varepsilon)/j_0'(\varepsilon)$ vs. ε for a single zirconium atom on a tungsten field emission tip. Comparison of experiment with theory. The top energy axis is taken with respect to a zero at the bottom of the tungsten conduction band, while the zero for the bottom axis is at the vacuum potential outside the tip.

appointment as a Distinguished Professor of Physics at the University of Tennessee and as a Distinguished Scientist in the Solid State Division of Oak Ridge National Laboratory. He has authored or co-authored more than 260 papers reporting on a wide variety of physical and chemical properties of surfaces and interfaces, as probed with a multitude of experimental techniques, always maintaining close coupling with theory. He received the 1983 Davisson-Germer Prize from the American Physical Society. Gadzuk remains at NBS/NIST, and for several years he was a "permanent" visiting professor jointly at NORDITA (Copenhagen) and Chalmers University (Goteborg). His research activities, resulting in over 150 papers, have been mainly in surface-related areas of theoretical atomic, molecular, solid state, and chemical physics, with special attention focused on the fundamental similarities existing in seemingly different fields of physics. He is currently interested in the dynamics of molecular processes at surfaces, particularly those aspects pertinent to the development of Femtochemistry at Surfaces involving hot electrons produced both by ultrafast lasers and by tunneling devices. He was a recipient of the Arthur S. Fleming Award, given annually to the ten outstanding young men and women in the U.S. Federal service. Following the resonance tunneling work, Young brought to fruition his scanning device for measuring surface topography which, as acknowledged by the 1986 Physics Nobel Committee, was a prototype of the scanning tunneling microscope. After abrupt termination of this project in 1971, Young remained at NBS in both a technical and administrative role, first as a Section Chief and then a Division Chief, directing NBS activities in mechanical metrology and robotics until his formal retirement in 1981. Since then he has actively pursued his interests as an inventor; as a private consultant to industry and government (including NIST) on topics in metrology, STM, vibration isolation, and instrument development; and as a grandfather and a sailor. In recognition of his invention of the Topografiner, in 1986 he received a Presidential Citation, and in 1992 he was presented the Gaede-Langmuir Award of the American Vacuum Society.

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