Scanning probe energy loss spectroscopy: Angular resolved measurements on silicon and graphite surfaces

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We report angle resolved ''scanning probe energy loss spectroscopy'' measurements from Si(111)-7×7 and graphite surfaces. Electrons incident on the surface after field emission from a scanning tunneling microscope tip are backscattered and detected with an energy and angle resolved hemispherical analyzer. We find that the reflected signal is sharply peaked in the direction parallel to the surface plane. Characteristic energy loss peaks corresponding to bulk and surface plasmon modes of the different surfaces are observed. © *2000 American Institute of Physics.* [S0003-6951(00)05551-0]

Spectroscopic, i.e., chemical, analysis is a key frontier in scanning probe microscopy. The scanning tunneling microscope (STM) offers outstanding spatial resolution but spectroscopic information is by comparison rather limited. Even the recent pioneering demonstrations of vibrational spectroscopy within the STM junction by Ho and colleagues[1,2] are restricted to cryogenic temperatures, since the energy resolution depends on kT, limiting the general applicability of this technique as a practical analytical tool. The goal of the research reported here is to combine imaging capabilities approaching that of the STM[3] with the kind of spectral information provided by electron energy loss spectroscopy (EELS) in reflection mode,[4,5] thus providing a tool for local spectroscopic surface analysis. In order to detect electrons reflected from the STM junction, the tip must be operated in field emission mode, thus sacrificing subatomic resolution; however, a spatial resolution of 3 nm has already been demonstrated in reflected current measurements[6] (without energy analysis). Here we report angle resolved ''scanning probe energy loss spectroscopy'' (SPELS) measurements from Si(111)-7×7 and graphite surfaces. The results demonstrate a sharp maximum in reflected signal intensity parallel to the surface plane, where a richness of spectral information is obtained; specifically, the excitation of bulk and surface plasmon modes providing chemical identification of the surface.

The collection of electrons backscattered from a surface after field emission from a tip (without energy analysis) was first demonstrated in the ''topografiner'' of Young *et al.*[7] which predated the invention of the STM. In 1987 Reihl and Gimzewski[8] reported a ''field emission scanning Auger microscope,'' operating at a tip voltage of 1000 V and tip–sample separation of a few hundred microns; energy analysis of the backscattered electrons revealed both plasmon losses and Auger transitions. These results were subsequently confirmed by Tomitori *et al.*[9] The detection of secondary electrons excited by a field emission tip has also been reported.[6,10] In a recent report, Festy *et al.*[11] explored the imaging possibilities provided by detection of the total current backscattered from the surface. The present work reports both angle and energy resolved measurements of the backscattered signal.

The experimental setup consists of a scanning tunneling microscope and a hemispherical electron energy analyzer housed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The STM is based upon the design of Lyding *et al.*[12] The analyzer is mounted on a rotatable base and rotates about the STMs tip in a plane perpendicular to the sample. The angular range covered is from $-0.8°$ to $18°$ ($\pm1.5°$) and is measured from the plane parallel to the surface. The silicon (111)-7×7 samples were prepared via direct resistive heating[13] while the highly oriented pyrolitic graphite samples were cleaned by electron bombardment heating.

Figure 1(a) shows an example of a SPELS spectrum obtained from the Si(111)-7×7 surface in UHV. The incident beam energy was 200 eV and the analyzer was oriented parallel to the surface plane. In addition to the well-defined elastic peak (full width at half maximum=1.5 eV)[14] apparent in the figure, a broad energy loss peak is evident in the spectrum above 10 eV. Marked on the figure are the bulk and surface plasmon peak energies for Si(111)-7×7.[15] The spectrum is remarkably similar to previous EELS results obtained with a conventional electron gun (normal to the surface) and a cylindrical mirror analyzer with a large acceptance angle;[15,16] in this case the analyzer integrates over the parallel component of the electron wave vector, $\mathbf{q}_{\parallel}$, leading to a broadening of the loss peaks. In our case, the acceptance angle of the hemispherical analyzer is well defined (3°), but the analyzer integrates over a range of electron trajectories from the tip (differing trajectories become indistinguishable when far from the tip apex). The shoulder in the energy loss spectrum, Fig. 1(a), above 20 eV may arise from multiple excitations. Spectra such as that shown in Fig. 1(a) are readily reproducible, even when the tip–sample separation is reduced from the micron range to 200 nm.

The surface specificity provided by the SPELS technique is further demonstrated by comparing the Si spectrum, Fig. 1(a), with Fig. 1(b), which shows a spectrum obtained from the graphite surface. The incident beam energy is 200 eV and the analyzer angle is again parallel to the surface plane. The

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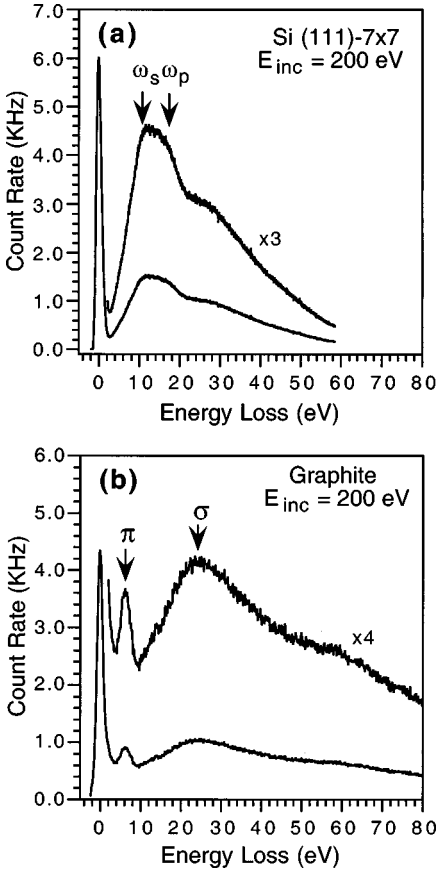

FIG. 1. (a) Scanning probe energy loss spectrum of a Si(111)-7×7 surface. The incident beam energy was 200 eV and the sample current was held constant at 15 nA. The analyzer angle was parallel to the surface plane. The bulk and surface plasmon energies of Si(111)-7×7 are labeled. (b) Scanning probe energy loss spectrum of a graphite surface. The incident energy was 200 eV and the sample current was held constant at 20 nA. The analyzer angle was parallel to the surface plane. The π and σ band plasmons of graphite are labeled.

SPELS spectrum for graphite is quite different from that of the Si surface. Two prominent energy loss peaks are clearly observed in Fig. 1(b), corresponding to the π and σ band plasmon modes at 6 and 25 eV. Once more the SPELS spectrum for graphite closely resembles an angle integrated EELS spectrum.[17] The weak shoulder at 50 eV in Fig. 1(b) may again be due to multiple excitations.

The spectra shown in Fig. 1 were obtained with the electron analyzer parallel to the surface; away from this direction, the reflected signal level, and hence the signal/noise ratio crucial for practical analysis, fall dramatically. Figure 2 shows SPELS spectra from the Si(111)-7×7 surface obtained at three different angles (all close to the surface plane; 0°, +1.4°, and −0.8°). One can see that the maximum elastic intensity occurs parallel to the surface and falls off in both directions (i.e., in front of and behind the surface). However, the fact that the spectral intensity above an energy loss of 20 eV detected behind the surface plane is greater than in front of the surface highlights the principle reason why we believe the backscattered electrons emerge so close to the surface; namely, the long range repulsive field arising from the bias voltage applied to the tip (here −200 eV) bends the trajectories of the backscattered electrons towards the surface (and even beyond the surface plane).[18] This effect

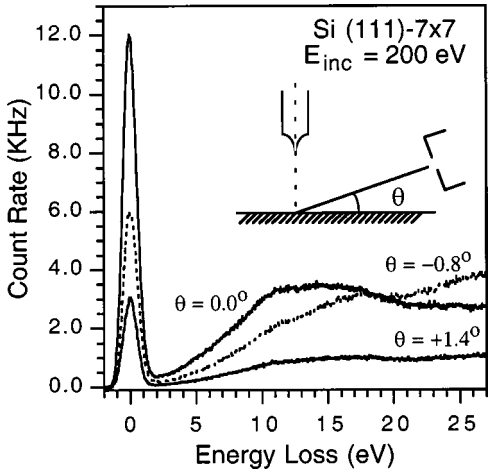

FIG. 2. Scanning probe energy loss spectra of Si (111)-7×7 for three different analyzer angles, −0.8°, 0.0°. and +1.4° with respect to the surface. The incident beam energy was 200 eV, and the sample current was held constant at 20 nA.

will be strongest for those electrons with the lowest kinetic energy, i.e., greatest energy loss.

Figure 3 displays SPELS spectra from the graphite surface, again as a function of analyzer angle (from the surface plane). In this case we have normalized the spectra according to the corresponding elastic peak intensities in order to highlight the changes in the relative intensities of the different loss features. Specifically, the energy loss intensity at large energy losses (notably at ≈65 eV) seems to be enhanced as the analyzer moves away from the surface plane towards the surface normal. One possible explanation for this behavior derives from the angular spread of the ''dipole lobe'' which describes the scattering cross section in the dipole scattering mechanism of EELS[19]

$$\Psi_E = \frac{\hbar\omega_s}{2E_0}, \tag{1}$$

where $\hbar\omega_s$ is the excitation energy, E_0 is the impact energy,

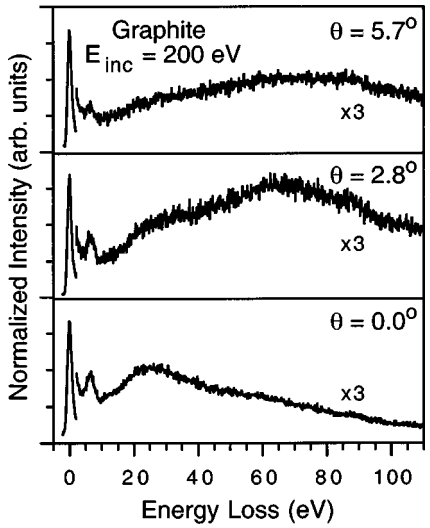

FIG. 3. Scanning probe energy loss spectra for the graphite surface for three different analyzer angles of 0.0°, 2.8°. and 5.7° with respect to the surface. The incident beam energy was 200 eV and the sample current was held constant at 30 nA. In this case the spectra have been scaled such that the elastic peak intensity appears the same at each angle.

and $_E$ is the angular width of the dipole lobe. One can see that the width of the dipole lobe increases with increasing energy loss, thereby ''spreading'' the angular distribution of these electrons further away from the surface. Note that this mechanism is in competition with the repulsive field caused by the tip.

In summary, we have reported measurements of the energy and angular distributions of electrons backscattered from the junction of a field emission STM. Distinctive energy loss features are observed from the Si(111)-7×7 and graphite surfaces when the analyzer is located parallel to the surface plane, where the signal levels peak sharply, an effect attributed to the long range repulsive field due to the bias voltage on the tip. Signal levels are sufficiently high to suggest that practical spectroscopic analysis of surfaces, with nanometer-scale resolution, should be possible.

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