Observations of Surface Temporal Fluctuations by Low Energy Electron Diffraction

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We present evidence for equilibrium temporal fluctuations in a high resolution low energy electron diffraction (LEED) experiment. These fluctuations are the reciprocal space analog of current fluctuations in field emission microscopy and therefore can be used to extract surface kinetic information. We show that even when the electron beam illuminates an area larger than its correlation length, time correlated data can be extracted from LEED. To demonstrate this, we present time dependent data from a W(430) surface, which reflects thermal step fluctuations. Our results illustrate the potential of LEED as a real time, ultrafast probe. [S0031-9007(98)07297-4]

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Real time surface kinetic information is crucial to the understanding of many important surface phenomena including diffusion, growth, 2D phase transitions, and many others [1]. Real space probes, in particular field emission microscopy (FEM) and scanning tunneling microscopy, have been used to obtain diffusion information [2,3]. In these experiments time correlations in the emitted current from the tip can be related to the movement of atoms into and out of a small probe area on the surface. These techniques require the use of high electric fields and therefore the role of electrostatic forces on surface kinetics becomes an important issue to be evaluated [4]. If an analogous technique could be developed in reciprocal space, kinetic information could be gained for a large variety of systems near equilibrium conditions. For convenient laboratory use, low energy electron diffraction (LEED) is the experiment of choice. But because the electron beam diameter is much larger than the finite correlation length (ζ) of a LEED beam, it is not clear whether the incoherent sum over 10^6 domains (where the area of a domain $= \zeta^2$) in a LEED experiment would average out any time correlations in the collected signal [5]. This has been one motivation to develop coherent x-ray sources by using small apertures to produce beams small enough to encompass a few domains [6].

In this Letter, we show that beam diameter is not the limiting parameter in a temporal LEED measurement. Instead, it is the probe current density that increases the true kinetics signal relative to statistical noise. Since current densities in LEED are very large ($\sim 10^{20}$ electrons/m^2), temporal measurements should be possible. To demonstrate that we have measured the temporal fluctuation from a W(430) surface that contains a high density of atomic steps using high q-resolution LEED. The motion of a step is clearly visible in the time autocorrelation function of the diffracted beam. Both temperature and wave vector changes distinguish these correlated fluctuations as being due to steps.

All the data presented here were taken with a high q-resolution LEED diffractometer described elsewhere [7]. The electron energy was kept fixed at 150 eV corresponding to a wavelength of 1.00 Å. The LEED transfer width was $\sim$1300 Å at the experimental geometry used in these experiments. Reciprocal space coordinates are given in terms of the conventional cubic unit cell with sides $a^* = 2\pi/a = 1.988$ Å^{-1}. The components of the momentum transfer, $q_\parallel$ and $q_\perp$, are measured parallel and perpendicular to the (110) plane, respectively. Cleaning procedures for the tungsten surfaces have been described elsewhere [8]. The stepped W(430) surface has a staircase structure consisting of (110) terraces of width $L = ma_\parallel = 15.64$ Å ($m = 7$ and $a_\parallel = a/\sqrt{2} = 2.23$ Å).

Data were accumulated with a digital counter that can acquire and store data with a gate time as low as 100 μsec without any interrupt ("dead time") for storing the signal on the computer. For the experiments presented below the actual gate time was 16.67 msec. Time series data were taken over 2000 to 10 000 gate periods.

The measured autocorrelation function $G(\tau)$ is defined as

$$G(\tau) = \langle \delta I(q,t) \delta I(q, t + \tau)_t . \quad (1)$$

Here $\delta I(q,t) = \langle I(q) \rangle_t - I(q,t)$, where $I(q,t)$ is the diffraction current (number of pulses in a gate period recorded by the electron multiplier) and the average in Eq. (1) is over time. In an actual experiment $G(\tau)$ is integrated at fixed wave vector q over a finite Δq defined by the instrument resolution ($\Delta q \sim 0.005$ Å^{-1}). For now we assume that Δq is sufficiently small so that we can ignore the integral. However, because of the strong q dependence of $G(\tau)$, discussed below, the q integration bears on the accuracy of determining $G(\tau)$. In a typical diffraction measurement the electron beam has a finite correlation length $\zeta = 2\pi/\Delta q$. Since the beam diameter D is much larger than ζ, the collected current is an incoherent sum over M domain, where $M \approx (D/\zeta)^2$. The beam diameter at the sample was measured to be 50 μm at FWHM. The beam diameter thus encloses $\sim 10^5$ domains.

$G(\tau)$ can be written in terms of the average autocorrelation function from a single domain, $G_p(\tau) = \langle \langle \delta I_{p,i}(t) \delta I_{p,i}(t + \tau) \rangle_t \rangle_i$. If the electron beam exposes

M incoherent domains, each domain will add as an incoherent sum to the total collected current as

$$\delta I(t) = \sum_{i=1}^{M} \langle I_p \rangle - [I_{p,i}(t) + \xi_i(t)]. \quad (2)$$

where $I_{p,i}(t)$ is the diffraction intensity from the ith incoherent domain and $\langle I_p \rangle$ is the average signal from each domain (i.e., $\langle I \rangle = M\langle I_p \rangle$). $\xi(t)$ is a noise source presumed to be purely statistical so that its autocorrelation function is $\langle \xi_i(t)\xi_j(t+\tau)\rangle = \langle I_p \rangle \delta_{i=j}\delta(\tau = 0)$. From Eqs. (1) and (2) the measured autocorrelation function is then

$$\frac{G(\tau)}{\langle I \rangle} = \delta(\tau = 0) + \frac{\langle I \rangle}{M} \frac{1}{\langle I_p \rangle^2} \{\langle \delta I_{p,i}(t)\delta I_{p,i}(t+\tau)\rangle_{i,t} + (M-1)\langle \delta I_{p,i}(t)\delta I_{p,j}(t+\tau)\rangle_{i\neq j,t}\}. \quad (3)$$

The last term can be dropped if there are no correlations between the scattering from different domains. The important conclusion of Eq. (3) is that the correlations can be measured as long as the second term is of order unity. Since M is proportional to D^2 (area of the beam), $G_p(\tau)$ can be measured regardless of the beam size for sufficiently large current density $\langle I \rangle / D^2$. It is important only that the current density and thus $\langle I \rangle$ be sufficiently large for the temporal diffraction signal to be measured.

To demonstrate that $G_p(\tau)$ can be measured, we have conducted a series of temporal diffraction experiments on W(430). On this stepped surface entropy favors the meandering of a step edge at elevated temperatures [9]. If we think of a step edge as a string, its shape (or "amplitude") fluctuates in time based on how atoms diffuse between sites on a step. The characteristic time for these fluctuations is based on interactions between adjacent steps as well as a number of possible rate limiting processes: attachment/detachment of atoms from the step edges, thermal diffusion of atoms across the terraces, or periphery diffusion of atoms along the step edges [10]. In a LEED experiment the measured intensity is due to the relative phase differences of an electron wave scattering from adjacent steps. As the step positions fluctuate in time, the relative phases between adjacent steps also fluctuate giving rise to temporal fluctuations in the diffraction intensities.

Time series data for the diffraction intensity from the W(430) surface were taken as a function of temperature and wave vector. The wave vector selection is critical since the sensitivity to step fluctuations can be tuned by the proper choice of $q_\parallel$ and $q_\perp$. At an in-phase condition, e.g., $q_\perp = a^*(3,3,0)$, adjacent steps scatter constructively and the diffraction intensity is insensitive to step fluctuations [11]. At this wave vector, $G(\tau)$ should represent only statistical noise [i.e., $G(\tau) = \langle I \rangle \delta(\tau = 0)$]. When $q_\perp$ is tuned to an out-of-phase condition, e.g., $q_\perp = a^*(2.5, 2.5, 0)$, adjacent terraces interfere destructively and the effects of step fluctuations on the diffracted intensity are at a maximum. At the out-of-phase condition the diffraction has a maximum intensity if $q_\parallel = a^*(1/2m, \overline{1/2m}, 0)$, where $m = 7$ for the W(430) surface. We have selected this value of $q_\parallel$ to collect the time series data and measure $G(\tau)$.

Figure 1 shows raw data for $G(\tau)/\langle I \rangle$ for both in-phase and out-of-phase wave vectors at $T = 711$ K. Note that $G(\tau = 0)/\langle I \rangle \approx 1.0$ for the in-phase $q_\perp$ as expected from Eq. (3). It is clear from the data that the in-phase $G(\tau)$ is essentially a $\delta(\tau = 0)$ function consistent with random noise with no time correlations as expected at this diffraction condition. Since the in-phase $G(\tau)$ shows no time structure, these data verify that nonrandom noise sources in the experiment are essentially zero for times greater than the gate period. At the out-of-phase diffraction condition the measured correlation function in Fig. 1 shows a strong time dependence that decays with a characteristic time constant.

Figure 2 shows $G(\tau)$ for the out-of-phase condition at two different sample temperatures. No decay is observed at 300 K and the value of $G(\tau = 0)/\langle I \rangle$ is again nearly 1.0 as expected for purely statistical noise. But when the sample temperature is increased to 989 K $G(\tau = 0)/\langle I \rangle = 2.35$ and the out-of-phase autocorrelation function in Fig. 2 again shows a characteristic decay. The observed wave vector dependence of $G(\tau)$ along with its temperature dependence clearly indicates that the source of the time fluctuations is from correlated motion of steps. These results conclusively demonstrate that temporal fluctuations can be observed with LEED.

We have also explored the temperature dependence of $G(\tau = 0)$. The data for both in- and out-of-phase $G(\tau = 0)$ are summarized in Fig. 3. More precisely, Fig. 3 is

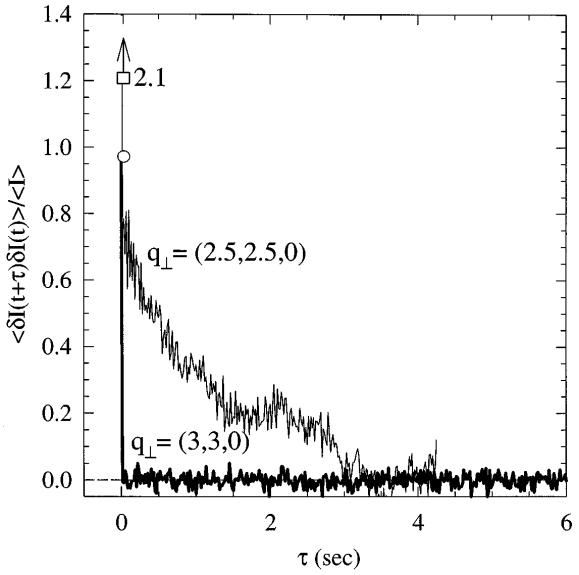

FIG. 1. The autocorrelation function $G(\tau)/\langle I \rangle$ vs time for both in-phase $q_\perp = (3,3,0)$ (heavy line) and out-of-phase $q_\perp = (2.5, 2.5, 0)$ (light line) wave vectors at $T = 711$ K. The $\tau = 0$ value of $G(\tau)/\langle I \rangle$ is marked with an "○" (in-phase) and "□" (out-of-phase) to show the delta function (statistical noise) term.

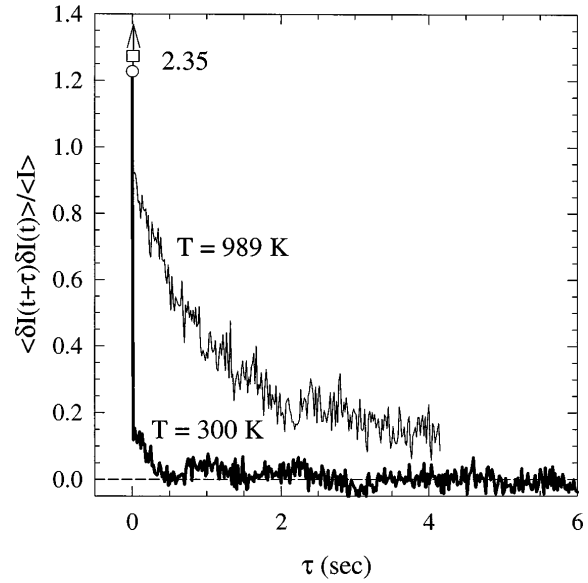

FIG. 2. The autocorrelation function $G(\tau)/\langle I\rangle$ vs time for the out-of-phase wave vector at 300 K (heavy line) and 989 K (light line). At 300 K $G(\tau)$ is purely statistical noise with $G(0)/\langle I\rangle$ being $\sim$1.0 (marked with an "○"). The $\tau = 0$ value for the 989 K data of $G(0)/\langle I\rangle = 2.35$ (marked with a "□" and is off scale).

a plot of $[G(\tau = 0)/\langle I\rangle - 1]/\langle I\rangle$, which from Eq. (3) is equal to $G_p(\tau = 0)/M\langle I_p\rangle^2 = \langle \delta I_p^2\rangle/M\langle I_p\rangle^2$, the mean squared intensity fluctuation due to a single domain divided by the number of domains. The two dashed lines in Fig. 3 represent the upper and lower statistical sample error if the signal was purely due to random noise. Nearly all of the in-phase data (open circles) fall within these limits indicating

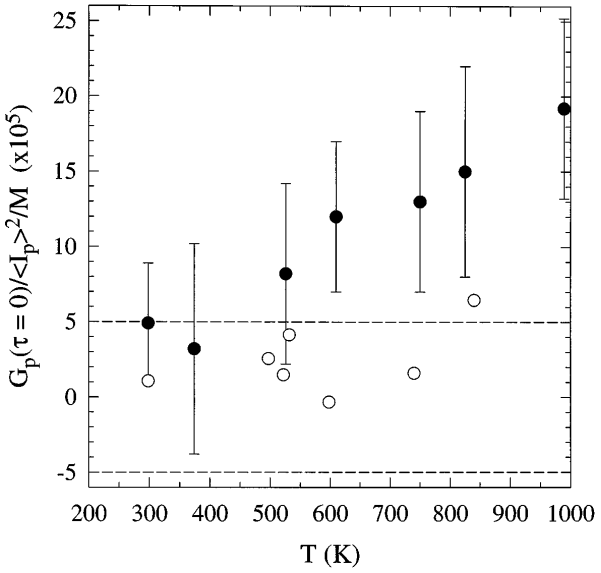

FIG. 3. The normalized autocorrelation function $G_p(0)$ as a function of temperature for in-phase (○) and out-of-phase (●) wave vectors. Dashed lines are statistical limits placed by acquisition sampling time and count rate.

that there is no temperature dependence of $G_p(\tau = 0)$ within the uncertainty of the experiment. Above 500 K the out-of-phase $G_p(\tau = 0)$ rises out of the noise region. As we show below, the temporal fluctuations increase with temperature because the mean squared step fluctuation is a strong increasing function of temperature.

As mentioned, the time decay of the measured autocorrelation function can give specific information about the kinetics of step motion. Previous work based on a Langevin analysis of reflection electron microscopy images was used to determine the mechanisms for step fluctuations on Si(111) [10]. In principle a similar analysis of LEED intensity fluctuations is also possible that would relate the physical parameters responsible for the fluctuations to specific properties of the autocorrelation function [i.e., time constant and functional form of the decay of $G(\tau)$]. At this point further theoretical development is necessary before this type of analysis can be carried out. We can, however, rationalize that the observed time constant of $\sim$1 sec measured from $G(\tau)/\langle I\rangle$ at 989 K in Fig. 2 is not unreasonable. FEM fluctuation experiments on vicinal W(320) have measured a self-diffusion coefficient of $D_s = 10^{-10}$ cm^2/sec [12]. This suggests that a typical time for an atomic event (i.e., attachment/detachment from a step) is $\tau_a \sim (a^2)/D_s \sim 10^{-5}$ sec. The large fluctuations in a step edge are built up from the collective motion of individual atomic events. Since fluctuations in the diffracted intensity can be measured with wavelengths up to the coherence length of the instrument ($\zeta = 1300$ Å), the time constant for collective motion of the step is $\tau_0 \sim \tau_a(\zeta/a)^2 \sim 1$ sec as observed. In addition step fluctuations on Si(111) have been measured at a temperature of 1173 K and are also on the order of seconds [10]. Assuming that an attachment/detachment mechanism is the rate limiting process on W(430) as it is for Si(111), our observed time constant of $\sim$1 sec is not unreasonable since the diffusion activation energy for W vicinal surfaces is slightly lower ($E = 0.9$ eV) [11] than the one for stepped Si(111) ($E = 1.0$ eV) [10].

While the time dependence of $G(\tau)$ cannot yet be related to atomic processes, the magnitude of the fluctuation [i.e., $G(0)$] can be derived from static equilibrium properties of the steps, specifically the mean squared displacement of a step. To show that the experimental results are indeed reasonable we have estimated $\langle \delta I_p^2\rangle/\langle I_p\rangle^2$ at $\tau = 0$ using a simple model for the diffraction from a stepped surface. Assume for simplicity that each step moves independently of the others (i.e., no step-step interactions). Let m be the number of atom rows in a terrace [$m = 7$ for the W(430) surface] and $\Delta(y)$ be the position of the step away from the $T = 0$ K position at a point y along the step. Let N_x be the number of steps in the beam ($\sim 10^4$) and let the spacing between rows in a terrace and the step height be denoted by $a_\perp$ and b, respectively. Then if the momentum vector at an out-of-phase condition is $q_\perp = \pi/b$ and $q_\parallel = \pi/ma_\perp$ and we assume that $\Delta(y)$ is independent of y, the diffracted amplitude is

$$A_p(q,t) = \frac{iN_y e^{i\pi/2m}}{\sin^2(\pi/2m)} \sum_{j=0}^{N_x-1} \cos[\Delta_j(t)\pi/m] + i\sin[\Delta_j(t)\pi/m]. \quad (4)$$

Since the total amplitude is a vector sum over N_x independent vectors in the complex plane, Eq. (4) represents a random 2D walker with $\tilde{x}$ and $\tilde{y}$ displacement variables given by $\cos(\Delta_j\pi/m)$ and $\sin(\Delta_j\pi/m)$, respectively. The intensity fluctuations then can be written in terms of $\langle\tilde{x}\rangle$ and $\sigma_x^2 = \langle\tilde{x}^2\rangle - \langle\tilde{x}\rangle^2$ [13]. As an estimate, we assume that Δ_j obeys Gaussian statistics with a mean squared deviation of $\langle\delta\Delta^2\rangle$. Assuming that $\langle\delta\Delta^2\rangle \ll (\pi/m)^2$ gives

$$\frac{G_p(0)}{M\langle I_p\rangle^2} = \frac{2\pi^4\langle\delta\Delta^2\rangle^2}{N_x m^4}. \quad (5)$$

Equation (5) illustrates two important points. First, the magnitude of the intensity fluctuations in a diffraction experiment is related to $\langle\delta\Delta^2\rangle^2$ and not $\langle\delta\Delta^2\rangle$ as would be expected in a real space measurement. Second, $G_p(0)$ measured at $(q_\parallel, q_\perp) = (\pi/b, \pi/ma_\perp)$ decays rapidly for surfaces with large terrace lengths (i.e., large m). Another way of expressing this is that, since $q_\parallel \propto \pi/m, G_p(0)$ is proportional to $q_\parallel^4$. It can be shown that this strong $q_\parallel$ dependence gives rise to 20% error in $G_p(0)$ because of the integration over the instrument resolution. It also means that care must be taken to reduce thermal drifts in the sample holder since they change $q_\parallel$ and thus further influence the accuracy of this technique.

To estimate $G_p(0)$ we use the Terrace-Step-Kink (TSK) model to describe the mean motion of a step with kinks of energy ε [14]:

$$\langle\delta\Delta^2\rangle_{\mathrm{TSK}} = \tfrac{1}{2}(\sinh[\varepsilon/2kT])^{-2}. \quad (6)$$

The kink energy for W(430) has been estimated previously, $\varepsilon \cong 90$ meV [15]. Using this value gives $G_p(\tau = 0)/M\langle I_p\rangle^2 \sim 9 \times 10^{-5}$ at 1000 K, which is within a factor of 2 of the experimentally observed value. This estimated signal should be compared to the statistical contribution to $G(\tau = 0)/\langle I\rangle^2$ in Eq. (3) (i.e., $1/\langle I\rangle$). Since our typical count rate at the out-of-phase peak was 8000 counts in the 16.7 msec gate time, the statistical contribution to the signal would be 1.2×10^{-4}. Based on the estimate above, the signal from the fluctuating steps is expected to be more than 40% of the total signal at 1000 K.

We have demonstrated that high q-resolution LEED can be used to obtain information on surface dynamics. The essential point is that the high count rates associated with electron diffraction allow even a small fluctuation to be measured with relatively high accuracy. Such diffraction experiments with very fast acquisition speeds (in principle limited only by the pulse width of the Channeltron detector $\sim$0.1 μsec) offer a great advantage over real space techniques since they can be performed selectively at different wave vectors. For example, reconstructed domain fluctuations can be monitored by selecting q on a superlattice rod while step fluctuations, as shown here, are measured by selecting a split peak at the out-of-phase condition.

An immediate application of this method is the measurement of surface diffusion coefficients (D_s) in interacting systems at equilibrium. Adsorbate diffusion causes density fluctuations in the adsorbate layer, leading to intensity fluctuations in the adsorbate superlattice spots. The autocorrelation function of the superlattice spot intensity can then be related to D_s. Since the density fluctuations are both generated and measured spontaneously in equilibrium, linear hydrodynamic theories can be used to compute the diffusion coefficient and compared directly with the fluctuation results. This is in contrast to diffusion measurement techniques that use sharp density profiles where it remains an open question on how to relate measurements to equilibrium calculations when severe nonlinear effects are present [16].

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