CREATION AND MOTION OF VACANCY ISLANDS ON SOLID SURFACES: A DIRECT VIEW

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By means of the Scanning Tunneling Microscope (STM), we have purposely created monolayer-deep vacancy islands on a Cu(111) surface covered with submonolayer amounts of Co and observed their motion in real time at room temperature. A quantitative evaluation of their random walk allows us to obtain their diffusion coefficient.

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Solid surfaces are by no means static. Adatoms move easily on compact metal surfaces. When there is no driving force, an adatom will perform a discrete, symmetric random lattice walk. The random walk of single adatoms [1] or small clusters [2] was observed with Field Ion Microscopy (FIM) already in the sixties. Recently, diffusion of single atoms [3] and concerted motion of atom [4] have also been viewed with STM. Here we report the purposeful creation of vacancy islands on a Co-modified, Cu(111) surface by means of STM; we image in a time-resolved manner their random motion at room temperature, their coalescence and their interaction with steps and screw dislocations. The diffusion of these objects can be visualized as a microscopic analog of the Brownian movement.

The experiments have been carried out on single-crystals of Cu cut within 0.2° of the (111) orientation, polished to mirror finish and cleaned by several hundred cycles of computer controlled sputtering and annealing. At the end of the process, the Cu(111) surface displayed straight monoatomic steps over more than 2000 Å, separating terraces 650 Å-wide on the average. The tip of the STM was a chemically etched, polycrystalline, tungsten wire.

In order to enhance the diffusion on the surface, cobalt was deposited at room temperature (RT) on Cu(111) by electron bombardment. At RT, Co decorates the steps of the original Cu (111) surface, produces triangular islands of bilayer height on the terraces [5] and forms a diluted, two-dimensional alloy in the rest of the surface by random substitution of Cu atoms in the first layer [de la Figuera et al., submitted to Surface Sci]. Since Co is 2% smaller than Cu, this surface alloying introduces a local stress field in the surface, which seems to reduce the activation barrier for diffusion.

The vacancy islands were created by transferring in a controlled manner atoms from the surface to the STM tip. This was accomplished by bringing the tip close to the surface (at chosen locations) and increasing the tunneling current from 1 nA to 10 nA with the feedback loop working at V=10 meV. At this demanded current, instabilities, faster than the feedback response time, set in and a sudden retraction of the z-piezo confirmed the transfer of atoms from the sample to the tip. The objects produced in this way were holes with hexagonal shape and monoatomic (2.0 Å) height, as indicated by line-scans (not shown). The size of these monoatomic-high vacancy islands can be controlled by adjusting the time of the tip residence in the chosen location. We have reproducibly produced islands with diameters ranging from 75 Å (involving 800 missing atoms) down to a few surface vacancies.

Subsequent to the creation of the vacancy islands, we followed the surface dynamics by recording STM images of a given area as a function of time during periods going from hours to days. The experiments reported here, performed at RT, have been selected to illustrate some of the phenomenology observed. The tunnelling conditions were V_S from -0.3 to -2 Volts and I_T =0.1-1 nA.

Fig. 1 shows snapshots of a movie illustrating the creation and RT diffusion of several artificially produced vacancy islands. The holes are made on a flat portion of the Co-modified surface surrounded by steps, decorated in turn by Co islands. An isolated triangular Co island appears at the upper left part of the terrace. The inmobile Co crys-
FIG. 1: Sequence of 480x480 Å² STM images of Co /Cu(111) recorded with $V_S = -0.15$ Volts and $i_T = 1$ nA. (a)-(c) movement at RT for three artificially produced vacancy islands. In (d) a fourth monoatomic-high hole is created on a pristine region of the surface. (e) and (f) show the subsequent diffusion of the vacancy islands. Each image has been recorded in 40 sec. The time interval from the first to the last image is 20 min.

tallites serve as marks to quantify the motion of the holes. The vacancy islands move considerably in the time scale between consecutive images. The average jump length is 10-20 Å for a typical time step of 60 sec. Their motion is not dependent of scan direction, set tunnelling current or sample voltage sign. This indicates that is not a field-assisted, tip-induced, diffusion effect [6][7]. The islands move as individual objects. In spite of the different scanning speeds in x (6000 Å/ sec) and y (12 Å/ sec) directions, the holes ba-

FIG. 2: Schematic plot of the diffusion paths of vacancy islands of different sizes obtained from the same sequence as Fig. 1.

sically keep their hexagonal shape in most of the images. The vacancy islands are not destroyed during their motion, which implies a collective behaviour of hundreds of atoms. This is in contrast to the behaviour of holes similarly-produced in Au(111)[8][9], where these tip-induced local perturbations of the stress distribution lead to large-scale atomic rearrangement [9] and the disappearance of the holes [8][9].

Fig. 2 reproduces the time evolution of the center of mass of several vacancy islands diffusing in a given area of the sample. The plot of their diffusion paths reminds us of the movement of pollen particles discovered in 1827 by R. Brown. Since the Brownian movement describes the motion of a macroscopic body arising from an unbalanced force caused by the bombardment of much smaller particles of the fluid in which the particle is suspended, it is illustrative to visualize the diffusion of these large vacancy islands at the Co-modified surface as a microscopic analog of the Brownian motion.

The Brownian motion is a particular example of the random walk problem which can be used as a simple model for diffusional processes. In a two
dimensional random walk, the mean square displacement, \( r^2 \) is \( 4Dt \), where \( D \) is the diffusion coefficient. In the Brownian motion, \( r^2 \) is of the same diffusional form with \( D = kT/A\gamma \), where \( A \) is the area and \( \gamma \) the viscous drag on the particle \( \gamma \). The mean square displacement of an individual vacancy island as a function of time is shown in Fig. 3a. It increases linearly with time, satisfying the statistical condition for random walk. An experimental verification of this linear dependence with diffusion time was already reported for individual tungsten adatoms as early as 1966 \( \text{[1]} \). In our case, the diffusion coefficient \( D \), calculated from the slope of plots that of Fig. 3a is of the order of \( 10^{-16} \text{cm}^2/\text{sec} \), changing by a factor of ten with the area of the particular vacancy island.

The dependence of the mean square displacement at fixed time with the area of the vacancy islands is shown in Fig. 3b. The displacement is roughly inversely proportional to the area of the islands. This is consistent with the predictions for a Brownian like motion \( \text{[10]} \).

When two vacancy islands come close enough during their random motion, they eventually coalesce. Fig. 4 shows such an event for two large (2000 and 610 missing atoms) vacancy islands. The process of coalescence conserves the area of the islands involved. The resulting island quickly orders to exhibit a hexagonal shape due to the reduction in step free energy which results from minimizing the total length of steps for a given area. This new island continues its random motion after coalescence.

Fig. 5 illustrates some additional phenomenology concerning the interaction of the vacancy islands with steps and dislocations. The sequence (a)-(c) shows that islands created close to a Co-modified, ascending step are reflected by the step, indicating that the step-island interaction is repulsive at short distances. Generally, the motion of the islands ended (after hours in some cases) by
Vacancy islands also can be created in clean Cu(111) by the procedure described above. In that case, however, holes produced at terraces or close to the straight steps of the clean crystal are almost completely inmobile at RT. For clean Cu(111), only the (shear) stress field present in the vicinity of screw dislocations induces a net displacement of the islands towards the dislocation core. Finally, the dislocation acts as a sink for the vacancy island. This behaviour, illustrated in Fig. 5 d-g, is consistent with the observation that impurities are generally attracted by dislocations [11].

In summary, we report the direct observation of the diffusion at RT of artificially created vacancy islands on a Co/Cu(111) surface. The presence of Co on the Cu surface is needed to lower the surface diffusion barriers. Work is in progress to identify the atomic processes responsible for the Brownian motion of the vacancy islands, such as creation and diffusion of kinks along the internal steps that constitute the borders of the vacancy islands.

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