# Toggling the local surface work function by pinning individual promoter atoms

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Atom by atom control over the local work function of a surface has been performed by using the tip of a scanning tunneling microscope to move and pin individual promoter atoms at predetermined atomic sites on the surface. Both positive and negative local work-function changes could be achieved, depending on the exact binding configuration of the pinned promoter atoms. This manipulation of individual promoter atoms has been exploited for testing the fabrication of atomic-scale chemical ''seeds.''

## I. INTRODUCTION

Since the pioneering work of Taylor and Langmuir,[1] adsorbed atoms have been known to modify the electron work function of a surface. This property relates to the change of electronic and/or atomic structure of a surface upon adsorption. It has important applications in many fields such as catalysis, ion propulsion, negative-electron affinity cathodes, thermoelectronic, photoelectric, and spin-polarized electron emitters, and ion sources for the neutral atom beams used in magnetic fusion devices.[2] Normally, the concept of work function is defined only at the macroscopic and mesoscopic scale.[3] In this paper we wish to explore the significance of using this concept when limited to a single promoter atom. Atomic-scale inhomogeneities of the local work function have been already evidenced, albeit indirectly, in metastable-quenching spectroscopy[4] and the photoemission of adsorbed xenon.[5] Here we investigate directly at the atomic scale with the scanning tunneling microscope (STM) the very subtle interplay between the various adsorption sites of individual promoter atoms and the positive- or negative-surface work-function changes. Furthermore, we demonstrate by using the manipulation capabilities of the STM that individual promoter atoms can be moved to predetermined surface sites, offering the prospect of toggling at will the surface work function at the atomic scale. In effect we now have control, atom by atom, over a macroscopic property. This opens the possibility of fabricating devices the size of a single or just a few atoms that will have properties specific to electron emitters, sensors, or chemical promotors.

A major difficulty in handling promoter atoms on semiconductors is their strong chemical bonding with the surface. A hydrogen atom adsorbed on a germanium Ge(111) surface was found to be the ideal model system since it can experience both positive and negative work-function changes due to the negligible polarity of the Ge-H bond.[6] Indeed it has been observed that the work function decreases upon low hydrogen coverage whereas it increases at higher hydrogen coverage.[6] We have revealed the origin of this very puzzling behavior by a STM atomic scale examination of the surface at various stages of the hydrogenation. At extremely low hydrogen coverage, individual adsorption sites (we shall call them ''triangle'' and ''square'' sites) account for the decreased work function. At higher hydrogen coverage, we have found new collective adsorption sites called ''zip'' sites

resulting from the adsorption of two separate hydrogen atoms that correlate with the increased surface work function. Quite interestingly, the two hydrogen atoms constituting the zip site can be separated by more than 100 Å. Furthermore, it will be demonstrated that one can selectively switch individual hydrogen atoms from one kind of adsorption site to another by using the tip of the STM as an atomic manipulator. This ability to switch the adsorption site and to displace individual hydrogen atoms in a controlled manner has allowed us to elucidate the exact atomic and electronic nature of each kind of adsorption site. It also provides us with a unique method to selectively toggle the change in the local surface work function from negative to positive values. As a further illustration of this new expertise, it will be shown that the manipulation of individual hydrogen atoms can be used to promote an oxidation reaction at any desired place of the Ge(111) surface.

## II. EXPERIMENTAL

Room-temperature scanning tunneling microscope (STM) experiments are performed in an ultrahigh-vacuum chamber ($p < 3 \times 10^{-11}$ Torr) where regular Ge(111) surfaces are prepared using the conventional method.[7] To prepare the clean surface, the heating of the sample is achieved by direct resistive heating. Over a period of 1 h the sample is slowly heated up to a temperature of 640 °C. The hot surface is then bombarded with 500-eV Ar ions (pressure $4 \times 10^{-6}$ Torr) and an ion current of 1 $\mu$A maintained for 30 min. The ion flux is at about 45° to the surface normal. After annealing at the same temperature for 1 h, the sample is then cooled down slowly over a further hour. Using samples that have an orientation less than 0.5° away from the (111) crystallographic direction, very large terraces (on average 3000 Å) are obtained by this preparation method. This implies that step atoms constitute less than 1% of the surface.

## III. RESULTS AND DISCUSSION

When exposed to atomic hydrogen using the procedure in Ref. 6, this surface exhibits features as shown in Fig. 1. At very low hydrogen coverage [0.009 and 0.016 ML, Figs. 1(a) and 1(b)], the majority of adsorption sites appear as triangles [see Fig. 2(a)] or squares [see Fig. 2(b)] made of bright adatoms. We have verified using STM manipulations that these
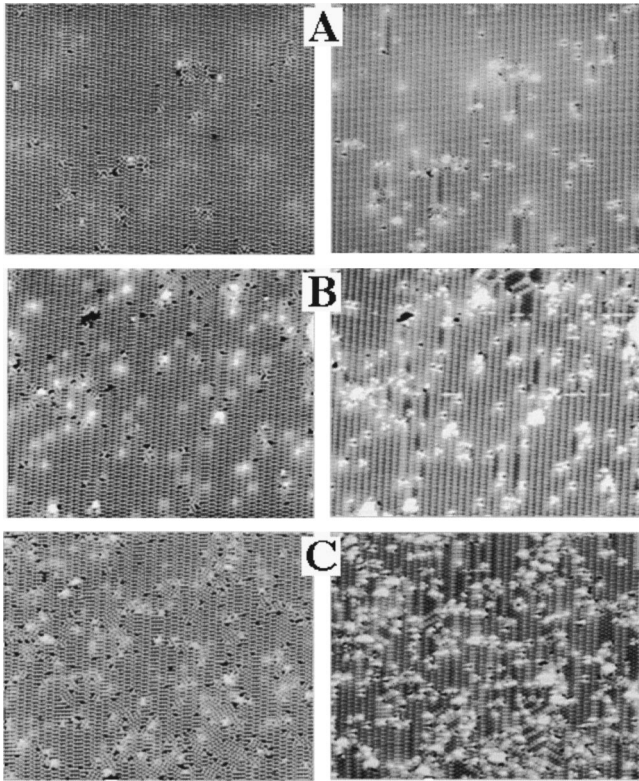
FIG. 1. STM topographs $(650 \times 545 \, \text{Å}^2)$ of a Ge(111)-$c(2 \times 8)$ surface after various exposures to atomic hydrogen. For each hydrogen coverage [(a) 0.009 ML, (b) 0.016 ML, and (c) 0.062 ML], the left STM topograph shows the unoccupied states ($I = 1$ nA, $V_s = 1$ V) and the right STM topograph shows the occupied states ($I = 1$ nA, $V_s = -1$ V) representing the same area.



FIG. 2. STM topographs of a Ge(111)-$c(2 \times 8)$ surface showing; in (a) a triangle and (b) a square site of a hydrogen atom adsorbed on a Ge rest atom surrounded by three and four adatoms, respectively, and in (c) a zip site produced by two hydrogen atoms. The left-hand STM topographs show the unoccupied states ($I = 1$ nA, $V_s = 1$ V) and the corresponding right-hand STM topographs show the occupied states ($I = 1$ nA, $V_s = -1$ V) of the same areas. To the right, the schematics of each site are shown where the Ge adatoms and rest atoms are represented as large and small light circles, respectively. Adsorbed H atoms are shown as dark circles and the effective charges are also indicated.

sites result from the adsorption of H atoms as has previously been suggested.[7,8] Possible contamination from the W filament used to dissociate the molecular hydrogen could be eliminated as blank experiments showed no new sites present. When increasing the hydrogen coverage [0.062 ML, Fig. 1(c)] the majority of sites appear as dislocations of a finite length along the adatom rows [Fig. 2(c)]. These sites, called ''zip'' sites, are associated with the movement of a row of adatoms into metastable $T_4$ sites.[9] Even though their exact structure and formation mechanism cannot be easily anticipated from the STM topographs alone, we will show that it can be deduced. An excellent correlation was found between the variation of the work function with the hydrogen coverage (Fig. 1) and the relative numbers of each type of site (Fig. 3). That is to say, the electron work function ($\phi$) decreases as long as the hydrogen adsorption sites are mainly triangle and square sites whereas $\phi$ increases when zip sites dominate. This strongly suggests that the former sites are associated with a local lowering of the work function and the latter one with a local increase of $\phi$. It is remarkable that the adsorption of a hydrogen can give rise either to a local lowering or increasing of $\phi$, depending only on the adsorption site.

To clarify this important observation, we used the tip of the STM as an atomic manipulator to selectively modify the hydrogen adsorption site. In the first experiment the STM tip
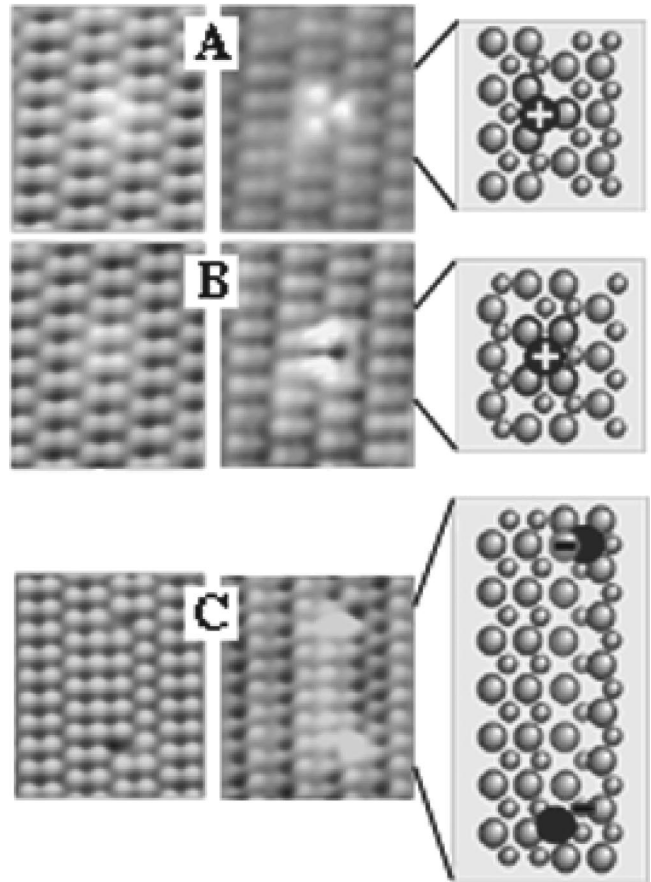
was used to displace a hydrogen atom from a ''triangle'' site to a ''square'' site [Fig. 4(a)]. The sequence of events to perform such a manipulation is the following. The tip is positioned over a triangle site. The feedback loop is swiched off, a positive voltage $V_s$ is applied to the surface and the tip-surface distance is adjusted to obtain an initial current at time $t = 0$ equal to any given value in the range 0.1–10 nA. The current is monitored as a function of time in order to provide the time $\tau$ at which the current suddenly changes due to the jump of the hydrogen atom from the surface to the STM tip. The feedback loop is switched on and the tip is moved with the H atom to the desired place on the surface. Then a procedure similar to the extraction is performed, however, with a negative voltage $V_s'$, to deposit the H atom on the surface. The triangle or square site nature of the new hydrogen adsorption site can be perfectly well controlled by positioning the STM tip over a rest atom surrounded by three or four adatoms, respectively. Detailed measurements of the
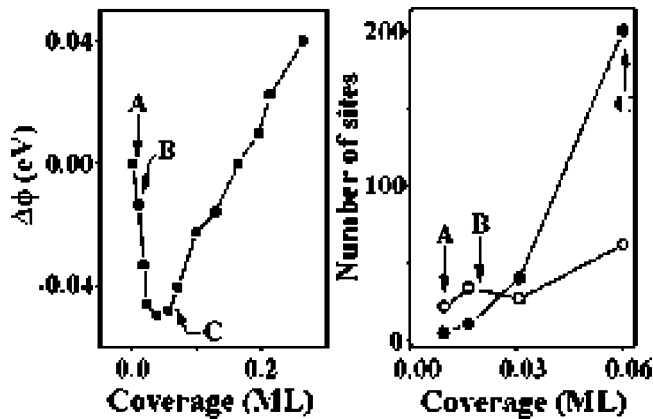
FIG. 3. (a) The measured work-function changes as a function of the hydrogen coverage as taken from Ref. 6. (b) The number of triangle plus square hydrogen sites (clear circles) and the number of zip sites (dark circles) over a $400 \times 400$ Å$^2$ as a function of the total hydrogen coverage. The letters $A$, $B$, and $C$ correspond to the coverages in Fig. 1.

extraction and deposition yields as a function of $V_s$, $V_s'$ and the initial current have been performed and will be discussed elsewhere.[10] For $V_s$ higher than 4 V, the probability of extraction is 100%. However, controlled deposition could be achieved only at voltages $V_s' < -4$ V and with a probability not exceeding 20%. Manipulations as shown in Fig. 4 clearly establish that triangle and square sites have the same origin and are due to the adsorption of an hydrogen atom on top of a rest atom surrounded by three and four adatoms, respectively. It also demonstrates our ability to pin a hydrogen atom at any predetermined rest atom site on the surface.

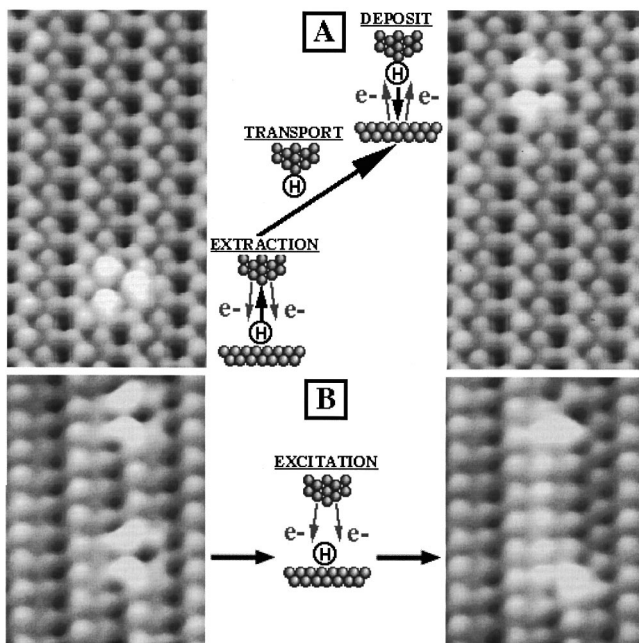Even more interestingly, we found it possible to use this



FIG. 4. STM manipulation of individual hydrogen atoms showing the transformation of (a) a triangle site into a square site and (b) two square sites into a zip site.

manipulation procedure to transform a triangle or a square site into a zip site, i.e., to locally modify the work-function change from a negative to a positive value. This is shown in Fig. 4(b). By applying a pulsed voltage $V_s = 3$ V with the tip during 50 ms to the H atom in the bottom square site [left topograph in Fig. 4(b)], we produced the zip site as observed in the right part of Fig. 4(b). This could be achieved only for $V_s \lesssim 4$ V. This transformation of a triangle or square site into a zip site was found to be much more probable than the hydrogen extraction whenever the initial triangle or square site was close to a similar hydrogen site located in the same rest atom row [as in Fig. 4(b)]. The zip site was found to consist of a displaced row of Ge adatoms which always ended either at another H adsorption site [as in Fig. 4(b)] or at a defect. Therefore, on surfaces having few defects and H sites, very long zip sites of up to 16 displaced adatoms could be produced by this method. It should be noted that, from time to time, the produced zip site was found to spontaneously return to the initial structure (two square or triangle sites). This indicates that the zip site corresponds to displaced adatoms with one hydrogen atom at each end without the removal or addition of any other atom. Zip sites produced either spontaneously by adsorption of H atoms (see Fig. 1) or by manipulation with the tip [see Fig. 4(b)] are thought to have the same structure since they appear identical in STM topographies both in the occupied and unoccupied electronic states. Similar zip sites have been observed after adsorption of $C_{60}$ molecules on Ge(111).[11] However, their exact structure, especially at each end, could not be identified. Here, the identification is made easier by the simplicity of the adsorbate (H) and by the manipulation sequence [Fig. 4(b)]. From a close examination of STM topographs in Figs. 2 and 4(b), we could deduce that the zip site is produced by the following tip-induced displacement of atoms. The hydrogen atom at the bottom of Fig. 4(b) (left), initially adsorbed on top of a Ge rest atom, is moved up on top of another Ge atom of the same second layer, which was initially bound to a Ge adatom. This Ge adatom, being destabilized, moves to an adjacent metastable $T_4$ site. This forces the whole row of six adatoms, up to the second hydrogen atom, to occupy metastable $T_4$ sites. As a consequence, the row of second-layer atoms (originally bound to adatoms) to the right of the modified row of adatoms become rest atoms and vice versa (see Fig. 2). The zip formation is energetically more favorable than the hydrogen extraction since it requires no bond breaking but only a hydrogen atom displacement followed by the displacement of adatoms along the row. This may explain why it is favored over the H extraction whenever two H atoms are adsorbed nearby along the same restatom row

In general, one defines the work function to be the work done to remove an electron from the Fermi level to infinity. At the macroscopic level, an analysis of the work function changes upon H adsorption has shown that it is the sum of three terms $\Delta\phi = \Delta\phi_{dip} + \Delta V_s + \Delta I_R$.[6] The surface Ge-H dipole contribution, $\Delta\phi_{dip}$ is expected to be negligible due to the comparable electronegativity of H and Ge atoms.[6] The $\Delta I_R$ part, related to the ionization energy change due to the reconstruction, is also considered to be either negligible or that it can be included in the $\Delta V_s$ term. Therefore, the mac-

roscopic work-function change was estimated to depend on the charge redistribution, resulting in a band-bending change of $\Delta V_s$.[6] At the atomic scale, our concept of the work function and band bending needs to be carefully thought through. For example, the accepted definition of the work function (as stated above) corresponds to some average over all atomic sites of the local barrier height (or local work function). Therefore, this idea of a local work function can be applied whatever the surface area under consideration, from the macroscopic scale down to the atomic scale. The local work function can be measured directly by microkelvin probes[12] with a micrometer resolution and by PEEM (Refs. 3) with a submicrometer resolution. Ideally, one could measure an apparent local barrier height, atom by atom, by doing $dI/dZ$ spectroscopy with the STM. However, first of all this quantity is not strictly equal to the work function.[13] Second, when doing tunneling spectroscopy at different sites, any observed change is conditional on many parameters, including changes in the atomic and electronic structures of both the surface and the tip, making it impossible to deduce any reliable value of the local barrier height. Moreover, In this case, $dI/dZ$ measurements are essentially impossible because the hydrogen is desorbed well before the voltage has been completed.

To understand at the atomic scale the redistribution of the local work function, one needs to consider the change in the effective charge on the various surface atoms. The adsorption of a hydrogen atom on a Ge rest atom, giving rise to a triangle or square site, is equivalent to a positive charge located at the rest atom site.[7] Indeed, the adsorption of the hydrogen atom saturates the occupied dangling bond of the rest atom. This effective positive charge is expected to induce a local screening by negative charges and consequently a local decrease of the work function,[7] which is what we have found. The zip case is more difficult to analyze. The hydrogen atom at the bottom end of the zip site of Fig. 2(c) inserts into a bond of an underlying Ge atom which, on the clean surface, was already bonded to a Ge adatom. This particular Ge adatom has been pushed up, releasing a new rest atom site equivalent to a negative charge [see Fig. 2(c)]. At the top end of the zip in Fig. 2(c), the hydrogen atom saturates the bond of an underlying Ge atom which should, in the absence of the hydrogen atom, be bonded to the sixth displaced Ge adatom. This results in a negative charge located on this last Ge adatom. Therefore, as indicated in Fig. 2(c), the zip site is equivalent to two negative charges located at each end of the zip. In short, the main difference in comparison with triangle and square sites, where hydrogen saturates rest-atom dangling bonds, is that in the zip site hydrogen atoms break adatom back bonds. The two equivalent negative charges of the zip site are expected to induce a local screening by positive charges, resulting in an increased local work function, as was deduced from the data in Fig. 1.

This ability to pin a hydrogen atom at a predetermined site on the surface and to modify the local work function has been used for testing the atomic-scale chemical encoding of the surface. It is indeed well known that the changes in work function upon adsorption of promoter atoms may enhance the surface chemical reactivity.[2] For example, it has
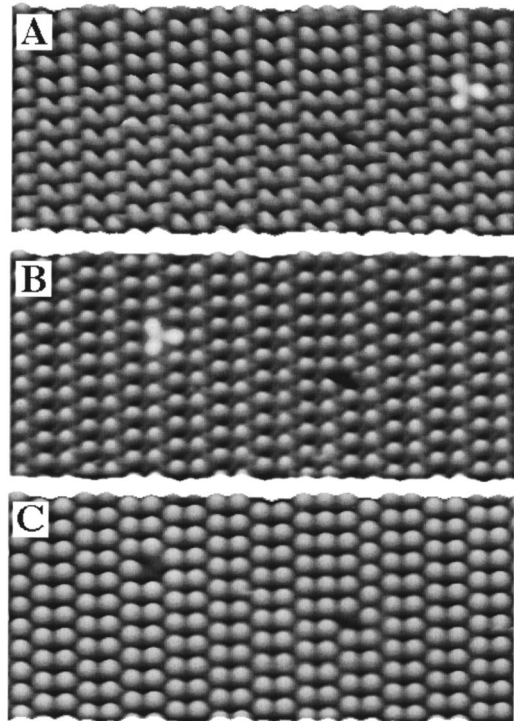


FIG. 5. Series of STM topographs ($I=1$ nA, $V_s=1$ V) showing the same area ($165\times90$ Å$^2$) of a Ge(111) surface after (a) adsorption of an hydrogen atom into a triangle site, (b) controlled displacement of the hydrogen atom to another predetermined triangle site, and (c) exposure to 20 langmuir of oxygen. The natural dislocation in all three topographs serves as a marker.

been observed that sodium atoms adsorbed on the Ge(111) surface can promote the reactivity of oxygen with this surface[14] which is normally completely inactive to oxygen.[15] By combining the manipulation of individual promoter atoms with their ability to locally trigger a chemical reaction, one can then expect to encode at the atomic scale the chemical reactivity of a surface. This is illustrated in Fig. 5 where a triangle hydrogen site [on the right side of Fig. 5(a)] has been displaced towards a chosen rest-atom site [on the left side of Fig. 5(b)] by using the STM manipulation procedure described above. The surface has then been exposed to 20 langmuir of $O_2$. It is seen in Fig. 5(c) that the only site on the surface which has reacted to oxygen is one of the bright adatoms surrounding the pinned hydrogen atom. This strong localization of the reactivity confirms that the change of electronic structure associated with the change of work function is very localized around the promoter atom. This experiment illustrates the use of pinning individual hydrogen promoter atoms to trigger the oxidation reaction at any desired place on the surface.

## IV. CONCLUSIONS

From our STM studies of the adsorption of atomic hydrogen on the Ge(111)-$c(2\times8)$ surface, we have observed two individual adsorption sites (''triangle'' and ''square'') at very low hydrogen coverage. As the hydrogen coverage is increased, we found a new collective adsorption site (''zip'')

resulting from the adsorption of two separate hydrogen atoms. We have been able to correlate these adsorption sites with the variation in the surface work function observed in previous experiments.[6] We have shown that we can selectively switch individual hydrogen atoms from one type of site to the other by manipulating them with the STM tip. This allowed us to toggle the change in the local work function. Furthermore, the manipulation of individual hydrogen atoms has been used to promote an oxidation reaction at any desired place on the surface. The manipulation of such promoter atoms with the STM opens up many other fascinating possibilities of encoding, at the atomic scale, the electronic properties of a surface. In particular, atomic scale active devices, like sensors or electron emitters, could be produced and tested by this method.

[1] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

[2] P. Soukiassian and H. I. Starnberg, in *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, New York, 1989).

[3] H. H. Rotermund, W. Engel, M. Kordesch, and G. Ertl, Nature (London) **343**, 355 (1990).

[4] J. Lee, C. Hanrahan, J. Arias, F. Bozso, R. M. Martin, and H. Metiu, Phys. Rev. Lett. **54**, 1440 (1985).

[5] K. Wandelt, in *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, New York, 1989).

[6] L. Surnev and M. Tikhov, Surf. Sci. **138**, 40 (1984).

[7] G. Lee, H. Mai, I. Chizhov, and R. F. Willis, J. Vac. Sci. Technol. A **16**, 1006 (1998).

[8] T. Klistner and J. S. Nelson, Phys. Rev. Lett. **67**, 3800 (1991).

[9] I.-S. Hwang, S. K. Theiss, and J. Golovchenko, Science **256**, 490 (1994).

[10] G. Dujardin, F. Rose, and A. J. Mayne (unpublished).

[11] K. R. Wirth and J. Zegenhagen, Surf. Sci. **351**, 13 (1996).

[12] M. Tanimoto and O. Vatel, J. Vac. Sci. Technol. B **14**, 1547 (1996).

[13] *Scanning Tunneling Spectroscopy*, edited by J. A. Stroscio and W. J. Kaiser (Academic, New York, 1993), p. 20.

[14] D. Jeon, H. W. Joo, T. Hashizume, and T. Sakurai, Appl. Phys. A: Mater. Sci. Process. **66**, S981 (1998).

[15] A. J. Mayne, F. Rose, and G. Dujardin (unpublished).