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Role of the dopant in silicon on the dynamics of a single adsorbed molecule

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We investigate the role of the dopant in silicon on the dynamics of a single adsorbed molecule. We demonstrate that the dynamics of a single bistable molecule, a biphenyl molecule, adsorbed on a Si(100)-(2×1) surface is markedly dependent on the silicon type of doping (p or n) even though the electronic excitation and relaxation processes are unchanged. Both strongly and weakly chemisorbed individual biphenyl molecules are shown to interact differently with p- or n-doped Si(100) surfaces, thus inducing different stabilities of the adsorption configurations and different molecular dynamics. These effects rely on electrostatic interactions between distributed charges inside the molecule and charged surface states. The described phenomenon, which is *a priori* general, should be applicable to most of the molecules adsorbed on doped semiconductors having surface states in their band gap. This result is anticipated to have important applications in molecular electronic for positioning individual molecules with precision.

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I. INTRODUCTION

Doping lies at the heart of semiconductor physics and technology.[1] Semiconductor optoelectronic devices have already reached the nanometer scale in the controlled spatial concentration of dopants.[2] The development prospects focus on implementing this semiconductor technology with single molecule operation.[2–5] Indeed, a number of optical, electronic, mechanical, and chemical functions have been recently demonstrated on single molecules.[6–16] In this paper, we show that the type of dopant (p or n) in silicon allows to tune the dynamics of a single bistable molecule, a biphenyl molecule adsorbed on a Si(100)-(2×1) surface. This effect relies on electrostatic interactions between charges distributed inside the molecule and charged surface states. This general phenomenon provides a method to control the movements of molecules adsorbed on semiconductor surfaces by using the semiconductor processing techniques.

II. EXPERIMENT

Clean Si(100) surfaces from n-doped (As, $\rho=0.004-6\ \Omega\ \mathrm{cm}$) or p-doped (B, $\rho=0.004-6\ \Omega\ \mathrm{cm}$) silicon substrates were prepared, as described elsewhere.[17] Biphenyl molecules were deposited on the Si(100) surface in the ultrahigh vacuum (UHV) preparation chamber while keeping the silicon sample temperature at 350–400 K (strongly chemisorbed configuration) or at 250 K (weakly chemisorbed configuration). The silicon sample was then cooled down to 5 K and transferred to a UHV low temperature scanning tunneling microscope (STM). All STM topographies and manipulations were carried out at 5 K.

III. RESULTS AND DISCUSSION

As reported earlier,[18–20] the biphenyl adsorption configuration can be selected by choosing the substrate temperature during deposition. At 350–400 K, biphenyl molecules adsorb in the strongly chemisorbed configuration, whereas at 250 K, biphenyl molecules adsorb in the weakly chemisorbed configuration. The exact transition temperature from the strongly to the weakly chemisorbed configuration is not known with precision. At room temperature (300 K), both the strongly and weakly chemisorbed configurations could be observed in the STM topographies.[20] Biphenyl molecules in the weakly chemisorbed configuration were unstable and were observed to oscillate through thermal activation at room temperature (300 K).[20] In their strongly chemisorbed configuration, biphenyl molecules were observed to be fixed at room temperature[20] and *a fortiori* at low temperature[18] during scanning with the STM. However, when adsorbed in the strongly chemisorbed configuration, the biphenyl molecule could be switched with tunneling electrons from one stable position (S_1) to the other (S_2) by applying a negative surface pulse voltage (−3 V) (Ref. 18) [see Figs. 1(a)–1(d)]. This is the so-called bistable configuration. Although some kind of thermally activated bistability has also been observed for the weakly chemisorbed configuration,[20] only the strongly chemisorbed configuration whose bistability is activated by electronic excitation is actually recognized as a bistable configuration.

The method for electronically inducing with the STM the molecular switching of the biphenyl molecule in its strongly chemisorbed configuration has been previously studied for p-doped Si(100) surfaces.[18] Here, we wish to investigate the role of the type of dopant in silicon on the properties of this bistable molecule, in particular, on its molecular dynamics. The STM topographies of the bistable biphenyl molecule (for any surface voltage in the −2 to +2 V range) are similar whatever the substrate type of dopant [see Figs. 1(e) and 1(f)], although the STM imaging of the Si(100) surface itself is known to depend on the type of dopant.[21] However, the molecular dynamics of the bistable molecule as probed by recording the tunnel current during the pulse voltage is markedly different for p-doped and n-doped silicon [see Figs. 1(g) and 1(h)]. Numerous peaks are observed in the tunnel current curve of the p-doped sample for time $t<t_{\mathrm{exc}}$, t_{exc} being the time of excitation before the molecule switches from S_1 to S_2. These peaks have been shown[18] to correspond to the movement of the molecule into a transient molecular con-

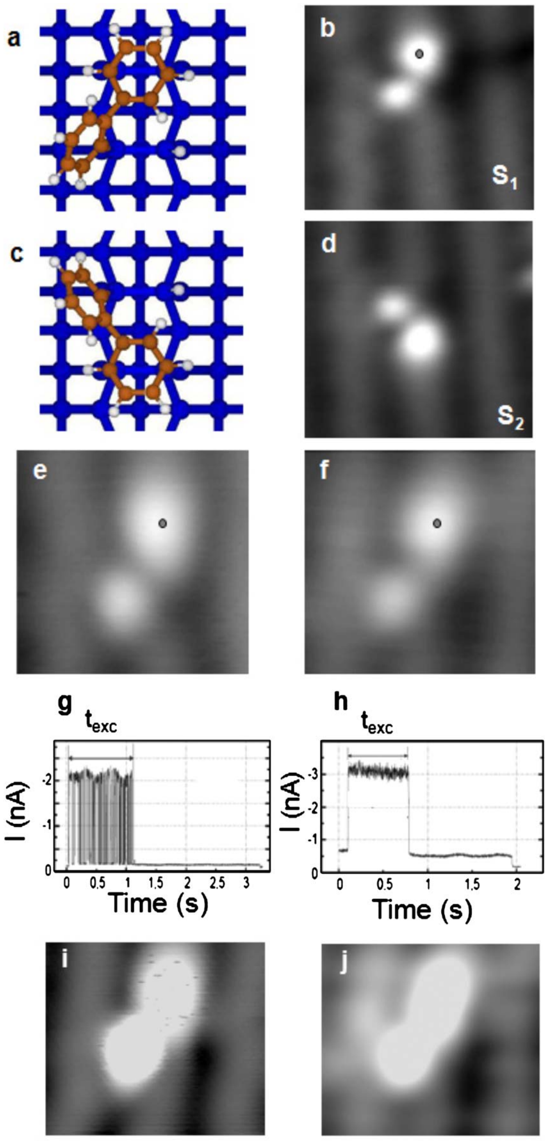

FIG. 1. (Color online) Role of the type of dopant in silicon on the bistable dynamics of biphenyl on Si(100). (b) and (d) are the STM topographies ($V_S=-2$ V, $I=0.2$ nA) of a single biphenyl molecule before (S_1) and after (S_2) switching on a *p*-doped Si(100) surface. The switching has been obtained by applying a negative surface pulse voltage (−3 V for 2 s) with the STM tip located at the dot position of (b). (a) and (c) are the schematic top view of the biphenyl molecule on Si(100) in the S_1 and S_2 conformations, respectively. (e) and (f) are the STM topographies ($V_S=-2$ V, $I=0.2$ nA) of a single biphenyl molecule in the S_1 conformation on a *p*-doped and an *n*-doped Si(100) surface, respectively. (g) and (h) are the tunnel current as a function of time during the pulse voltage for a *p*-doped and an *n*-doped Si(100) surface, respectively. The drop of the tunnel current at time t_{exc} is due to the switching of the molecule from S_1 to S_2. (i) and (j) are the STM topographies ($V_S=-2.5$ V, $I=0.2$ nA) of a single biphenyl molecule in the S_1 conformation on a *p*-doped and an *n*-doped Si(100) surface, respectively.

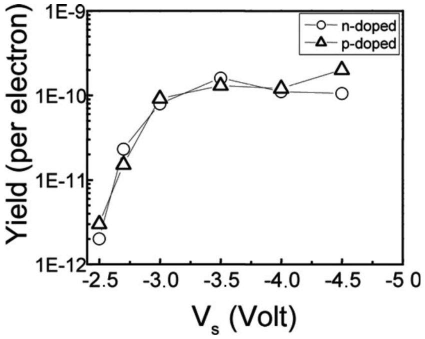

FIG. 2. Comparison of the switching yield (per electron) of a biphenyl molecule as a function of the surface voltage for *p*-doped and *n*-doped Si(100). Error bars are included in the size of the triangles and circles.

figuration *T* which is too unstable to be imaged with the STM. We emphasize that direct evidence of the existence of the *T* transient configuration could be obtained by rapidly scanning the STM tip along a single line scan.[18] From the width of the peaks in Fig. 1(g), the time the molecule adsorbed on the *p*-doped silicon spends in the *T* transient state has been found to be in the range 1–100 ms depending on the tunnel current and surface pulse voltage. These peaks can also be seen as black dashes in the STM topography when recorded at a lower surface voltage [Fig. 1(i)]. Surprisingly, no evidence of the transient *T* molecular configuration could be observed with *n*-doped silicon [see Figs. 1(h) and 1(j)] whatever the tunnel current and surface pulse voltage. Considering the bandwidth of our tunnel current detection (below 1.3 kHz), we deduce that the time the molecule spends in the transient *T* state is at least 2 orders of magnitude smaller for *n*-doped than for *p*-doped silicon. This type of dopant effect is very reproducible as the experiments have been repeated several times with different STM tips and samples.

The absence of any detectable molecular transient state (*T*) in the case of the *n*-doped silicon is indeed a puzzling problem. *A priori*, it can be due either to different electronic excitation and/or relaxation processes of the bistable biphenyl molecule or to a different stability of the *T* molecular state when going from *p*-doped to *n*-doped silicon. To compare the electronic excitation and relaxation processes of the molecule, we have measured the switching yield $Y(S_1 \rightarrow S_2)$ for switching the molecule from the S_1 state to the S_2 state as a function of the surface pulse voltage for both *p*-doped and *n*-doped silicon (see Fig. 2). The similitude between the two curves in Fig. 2 has important consequences. The threshold energy of the switching yield curves at 2.7 eV (Ref. 18) is the energy of the molecular resonance involved in the electronic excitation process. This means that the resonance has the same energy relative to the silicon Fermi energy for both *p*-doped and *n*-doped silicon. This can be understood by considering Fermi level pinning by the surface states.[22] The intensities of the two yield curves in Fig. 2 are also similar. This indicates that the whole sequence of electronic excitation and relaxation molecular processes for switching the molecule from S_1 to S_2 is identical for both types of silicon doping. One can anticipate that, similarly, the electronic processes for switching the molecule from S_1 to the transient *T* state are identical for *p*- and *n*-doped silicon (although this cannot be directly measured since the *T* state is not visible

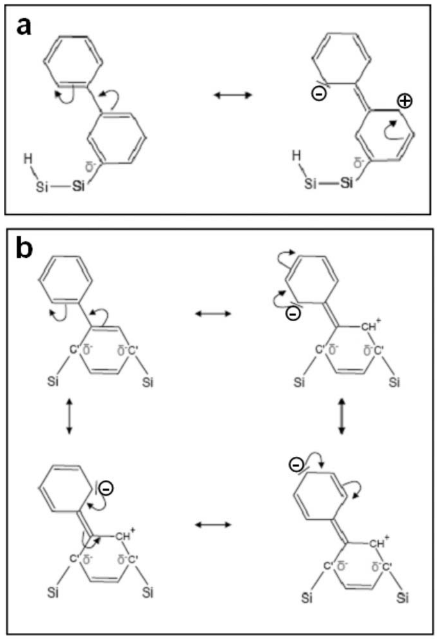

FIG. 3. Adsorption configuration of a biphenyl molecule on Si(100) in the T state of the (a) strongly chemisorbed configuration and in the (b) weakly chemisorbed configuration. Repartition of charges inside the molecule is shown in each case. All the resonance structures indicate a negative charge on the free phenyl ring.

with n-doped silicon). As a consequence, the absence of detectable T states in the tunnel current with n-doped silicon [Fig. 1(h)] is assigned to a decreased stability of the biphenyl molecule in its T state when adsorbed on n-doped silicon.

The unchanged stability of the S_1 and S_2 biphenyl molecular configurations and the decreased stability of the T configuration with n-doped silicon are believed to be related to the negative charging of surface states.[3,23] This induces a surface electric field which is likely to influence the stability and the dynamics of the molecule in its T configuration. Indeed, in the S_1 and S_2 configurations, both phenyl rings of the biphenyl molecule are considered to be strongly chemisorbed to the surface.[18,19,24] One phenyl ring (fixed phenyl ring) is strongly bound through a single Si-C bond with a dissociated hydrogen atom bound to the neighbour silicon atom (Si-H bond). The second phenyl ring (mobile phenyl ring) is chemically bound to the Si(100) surface in the butterfly configuration through two Si-C bonds.[18,19,24] Therefore, the molecule is strongly bound to the surface when adsorbed in the S_1 and S_2 configurations and is unlikely to be influenced by the surface electric field. This has to be compared with the molecule in the T transient configuration [Fig. 3(a)]. In this case, only one phenyl ring (fixed phenyl ring) is chemically bound to the surface through a Si-C bond. The second phenyl ring (mobile phenyl ring) is not chemically bound to the surface and will therefore undergo the influence of the surface electric field.[24] This effect is expected to be markedly increased by the negative charge on the mobile phenyl ring. Indeed, as shown in Fig. 3(a), the polarization of the Si-C bond (which bound the fixed phenyl ring to the surface) induces a negative charge on the carbon atom and this is balanced by the delocalization of a negative charge on the mobile phenyl ring. The repulsive interaction between this negative charge located on the mobile phenyl ring and the negative surface charge explains the decreased stability of the T configuration of the biphenyl molecule with n-doped silicon. On p-doped silicon, the charge of surface states is somehow more controversial. A downward band bending, associated with a positive charging of surface states, has been detected at low temperature on p-doped substrates but was attributed to a small density of surfaces states which could originate from defects.[25] Since our surfaces have a very low density of defects, the surface states on p-doped substrates are likely to be neutral. In any case, the T configuration is expected to be more stable on p-doped silicon than on n-doped samples, as it is observed experimentally. It is interesting to note that the type of dopant modifies the interaction between the molecule in its T configuration and the surface whereas it does not seem to affect the measured electronic excitation processes (threshold energy and yield). This can be explained by the fact that the potential energy surface representing the surface dynamics of the molecule must have a very shallow minimum for the T configuration. Since all experiments are performed at 5 K, a very slight change of a few meV of this minimum energy would be sufficient to explain the change of stability observed when changing the type of dopant. Such a small change of the interaction between the molecule and the surface might as well have no measurable effect on the electronic excitation processes.

In order to further test our model of electrostatic interaction between distributed charges inside the molecule and charged surface states, we have investigated the interaction of the weakly chemisorbed biphenyl molecule with p- and n-doped silicon surfaces. The weakly chemisorbed configuration has been assigned[19] to one phenyl ring strongly interacting with the Si(100) surface through two Si-C bonds in the butterfly configuration[26] and the second phenyl ring having no chemical bond with the surface. As shown in Fig. 3(b), this configuration is somewhat similar to the T state of the strongly chemisorbed configuration [Fig. 3(a)]. In both cases, the unbounded phenyl ring is expected to bear a negative charge due to the polarization of the Si-C bonds and the conjugation inside the molecule. It is therefore interesting to investigate the influence of the type of dopant on the stability of the weakly chemisorbed configuration. The weakly chemisorbed biphenyl molecule does not exhibit any bistable movement but rather diffuses across the surface when it is electronically excited ($V_S < -2$ V) with the STM tip.[27] This is mainly due to a weaker interaction with the surface as compared to the strongly chemisorbed configuration. However, under imaging conditions ($-2\text{ V} \leq V_S \leq +2\text{ V}$), the weakly chemisorbed biphenyl molecule does not diffuse across the surface and can be imaged with the STM, as shown in Fig. 4. In this case, the STM topographies are completely different on p- and n-doped silicon, indicating that the molecule interacts differently with these two surfaces. On the p-doped surface, the weakly chemisorbed biphenyl molecule appears as a bright spot centered on the silicon dimer line and some faint but fixed features nearby [Fig. 4(a)]. The bright spot is assigned to one phenyl ring chemisorbed in the butterfly configuration similar to the case of benzene[26] and the faint feature to the second phenyl ring

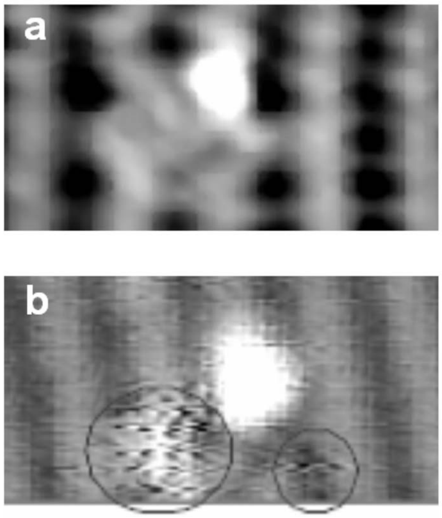

FIG. 4. STM topographies ($V_S = -2$ V, $I = 0.3$ nA) of a biphenyl molecule weakly chemisorbed on (a) a *p*-doped and (b) an *n*-doped Si(100) surface. The spiky appearance of some parts (surrounded by circles) of the STM topography of the molecule adsorbed on the *n*-doped Si(100) surface (b) indicates some movement of the molecule during the scanning.

interacting weakly with the surface. On the *n*-doped silicon surface, the STM topography appears again as a bright spot, but the faint feature nearby appears with dark dots, indicating that this part of the molecule is moving during the STM scanning, due either to electronic excitation or to some electric field effect [Fig. 4(b)]. This STM topography is assigned to the same adsorption configuration as for the *p*-doped surface, i.e., one phenyl ring strongly chemisorbed (bright spot) and a second phenyl ring in weak interaction with the surface. However, the spiky appearance of the second phenyl ring indicates that its interaction with the surface must be weaker than on the *p*-doped surface. The stronger interaction of the second phenyl ring with the *p*-doped surface is confirmed by the observation of buckled silicon dimers in the vicinity of this phenyl ring. The increased instability of the weakly chemisorbed biphenyl molecule on *n*-doped silicon is similar to that of the transient *T* state of the strongly chemisorbed bistable biphenyl. The explanation is also similar, i.e., a repulsive interaction between the negative charge of the weakly interacting phenyl ring [see Fig. 3(b)] of the molecule with the negative charge of surface states of the *n*-doped silicon.

We note that these differences between weakly chemisorbed biphenyl molecules on *p*- and *n*-doped silicon could not be observed in previous experiments.[20] Indeed, *p*-doped silicon was studied only at room temperature where the weakly chemisorbed biphenyl molecules oscillate under thermal activation.[20] The *n*-doped silicon was studied at low temperature, however, with a low spatial STM resolution.[20]

IV. CONCLUSION

In conclusion, the dynamics of a single bistable biphenyl molecule adsorbed on a Si(100) surface has been shown to be strongly dependent on the type of dopant in silicon. Although the electronic excitation and relaxation processes for switching a single bistable molecule are similar for both types of dopant, the stability of the transient *T* molecular state is much reduced for *n*-doped silicon as compared to *p*-doped silicon. This is ascribed to a repulsive interaction between a negative charge on the mobile part of the biphenyl molecule with the negatively charged surface states of the *n*-doped surface. A similar phenomenon has been observed in the STM topographies of the weakly chemisorbed configuration of biphenyl molecules which exhibit instabilities in the case of the *n*-doped silicon. This phenomenon is different from the influence of the type of dopant previously observed at the macroscopic scale in silicon etching[28] or in the adsorption of Li atoms on the Si(111):H surface.[29] In the former case, the chemical etching of highly boron doped silicon is stopped due to the shrinking of the barrier height for the penetration of electrons into the silicon substrate.[28] In the latter case, the specific adsorption sites of Li atoms observed for *n*-doped silicon are assigned to the decreased electrochemical potential of *n*-doped silicon as compared to *p*-doped silicon. Here, we have investigated the influence of the type of dopant at the level of a single molecule. The most surprising result is that the type of dopant does not affect its electronic properties (electronic excitation and relaxation) but rather its molecular dynamical properties through electrostatic interactions with charged surface states. In addition to its fundamental interest, this phenomenon, which enables to select the dynamics and the adsorption stability of individual molecules by tuning the type of dopant of a silicon surface, may have very important applications. By using the semiconductor industry processing techniques, one can pattern silicon surface areas of different types of doping (*n* and *p*).[23] This could be used, for example, to adsorb molecules at selected locations or to guide the movement of molecules along selected paths across a surface. In the context of molecular electronics, new methods for accurately positioning individual molecules can be anticipated.

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