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Hydrogen diffusion on Si(001)

J. H. G. Owen, D. R. Bowler,* C. M. Goringe, K. Miki, and G. A. D. Briggs
Department of Materials, Oxford University, Parks Road, Oxford OX1 3PH, United Kingdom

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We have imaged hydrogen on Si(001) at low coverages in a variable-temperature STM from 300 K up to 700 K. Individual hydrogen atoms were imaged which became mobile at around 570 K. The observed rate of hopping along the dimer rows was consistent with an activation energy of 1.68 ± 0.15 eV. Motion across dimer rows was rarely observed, even at the higher temperatures. The diffusion barrier for motion along the dimer rows has been calculated using tight-binding and density-functional theory in the generalized gradient approximation (GGA). The calculated barrier is 1.65 eV from tight binding and 1.51 eV from GGA. [S0163-1829(96)07543-1]

I. INTRODUCTION

The motivation for this study is twofold. First there is the intrinsic scientific interest in the adsorption and desorption behavior of hydrogen. Second, hydrogen plays an important role in the growth of silicon and silicon-germanium from hydride precursors; silicon growth is limited by the hydrogen desorption rate[1] as adsorbed hydrogen blocks the adsorption sites of disilane, although growth can still proceed slowly on a saturated surface.[2] Small amounts of surface hydrogen influence the silicon diffusion rate,[3] which will affect the reaction of disilane fragments to form epitaxial dimers.

The Si(001)-(2×1) surface is made up of silicon dimers with a strong σ-bond and a weak π-bond between them.[4] When atomic hydrogen chemisorbs, it does so by breaking the π-bond, and forming a strong Si-H covalent bond. The breaking of the π-bond costs about 0.2–0.3 eV,[5] and so it is energetically favorable for two hydrogens to adsorb on the same dimer. However, this requires surface mobility during or after chemisorption. Theoretical studies of this system,[6,7] (and this work) find that the activation barriers to diffusion are too large for significant motion at room temperature. In his experimental studies, Boland[8] found that for low coverages (about 0.08 ML), the hydrogen adsorbed randomly and singly at room temperature, but that a brief anneal to 630 K was sufficent for a sharp decline in the number of unpaired hydrogens. However, Widdra *et al.*[9] found that for hydrogen coverages between 0.1 and 0.8 ML, almost all the hydrogen pairs up upon adsorption, independent of temperature, from 150 K up to 600 K. They explain this observation with a mobile-precursor chemisorption mechanism (similar to that proposed by Sinniah *et al.* for desorption[10]) where the incoming hydrogen is initially in an excited band state, and so is able to sample several sites before final chemisorption in a favorable one. The delocalized hydrogen would have a limited range, and so this mechanism would not produce complete pairing at sufficiently low coverages of hydrogen.

Previous theoretical calculations of the diffusion barrier have been motivated by a desire to understand the desorption process. Two methods have been used: local density approximation (LDA), and configuration interaction (CI) with Stillinger-Weber potentials fitted to the result. Vittadini *et al.*[6] used LDA, and found a barrier of 1.3 eV along the dimer rows, and 1.8 eV across them. Wu and Carter[7] used CI methods, giving a value of 2.0 eV along the rows, and 2.7 eV across the rows. As these calculations did not allow substrate relaxations, they give an upper bound to the barrier. In order to estimate the effect of substrate relaxation, Wu, Ionova, and Carter[7] fitted a Stillinger-Weber potential to their CI calculations, and obtained a barrier of 1.65 eV along the dimer rows and 2.7 eV across them.

We have imaged the motion of individual hydrogen atoms at elevated temperature in order to estimate the diffusion barrier, and performed tight-binding, LDA, and GGA calculations of the same barrier. In Secs. II and III of this paper we describe the experimental and theoretical details, in Sec. IV we present our STM observations, in Sec. V we compare our theoretical calculations with our experimental and other theoretical results, and in Sec. VI we draw our conclusions.

II. EXPERIMENTAL DETAIL

A JEOL JSTM-4500XT elevated-temperature STM was used, capable of operation up to 1500 K. The base pressure of the system during the experiment was 1.1×10^{-10} Torr (as measured by the mass spectrometer), the majority of which was hydrogen. The sample was heated directly by passing current through it, and its temperature was measured using an infrared pyrometer whch reads from 570 K to 880 K, with a systematic error of 10 K and a random error of ± 20 K. The pyrometer was first calibrated against the eutectic temperatures of gold and aluminum on the surface of silicon, and was then used to plot a power-temperature curve ($P=aT+bT^4$). Below the range of the pyrometer, temperatures were estimated by extrapolation of the curve to 300 K.

The silicon wafers used were n-doped 0.1 Ω cm; they were cut into samples 1 mm by 7 mm and cleaned with a sulfuric acid/hydrogen peroxide etch. In UHV, they were cleaned by repeated flashing to 1400 K, followed by a slow cool from 900 K down to the desired temperature. This procedure repeatably gave a well-ordered surface, with the surface defect density dependent upon the rate of the slow cool.

All images were taken using a tungsten tip, keeping the tunneling current below 0.1 nA, and with sample bias voltages around -1 V; preliminary images of the clean surface were taken before dosing. The hydrogen dose was 99.99%

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H_2, with a small amount of water from the gas line, and was cracked by a tungsten filament located about 3 cm from the sample. The tip was mechanically withdrawn during dosing. After dosing, images were typically achieved within 5–15 min. An optimal number of adsorbates (about 50 per picture) was obtained by using very small initial doses, which were slowly increased.

Since we are interested in dynamic events, the atomic speed which can be measured in the STM is important. There are in general three regimes: a lack of any motion over many atoms, over long time scales such as 1 h; motion on the time scale of a picture, a few hops in 10 sec–1 min; and motion on the time scale of a scan line, a few hops in $\frac{1}{50}$ second. This gives a range of speeds from about 10^{-5} up to 10 hops/atom/sec.

III. THEORETICAL DETAIL

Initial calculations were performed in the tight-binding approximation, using the density matrix method of Li, Nunes, and Vanderbilt,[11] in an implementation by Goringe.[12] The hydrogen-silicon interactions were modeled using a nearest-neighbor parametrization of Bowler *et al.*,[13] which accurately reproduces long, hydrogen-silicon bonds by comparison with GGA calculations. The computational slab was one dimer wide, six dimers long and 10 layers deep. The bottom surface was terminated with hydrogen, and the lower five layers were constrained to be in bulklike positions; a total of 145 atoms were used.

Diffusion pathways were identified by constraining the hydrogen's position in the direction parallel to the dimer row. The minimum energy configuration was used for the start and end points, with the hydrogen on the ''down'' atom of a buckled silicon dimer. Three midpoint configurations were considered in terms of the buckling of the dimers: hydrogen between two ''up'' atoms, between ''up'' and ''down'' atoms, and between two ''down'' atoms. As the dimers on the surface flip rapidly between the two signs of buckling, diffusion will be dominated by the combination which results in the lowest energy barrier. This was found to be the configuration with the hydrogen between two ''up'' atoms.

The initial and minimum energy midpoint configurations were then rerelaxed using the density-functional theory computer code CASTEP,[14] with gradient corrected energies[15] evaluated using the self-consistent LDA charge density (''post-hoc GGA'').[16,17] The computational slab was two dimers wide, two dimers long, and five layers deep. The bottom layer was terminated with hydrogen, and constrained to lie in bulklike positions; a total of 58 atoms were used. Kerker pseudopotentials[18] in the Kleinman-Bylander form[19] were used, with an energy cutoff of 200 eV. This cutoff has been previously shown to give sufficient energy difference convergence.[20] The special k-point (0,0.25,0) was used. Our tight-binding calculations predict a minimum energy barrier of 1.65 eV. Our LDA DFT calculations gave a barrier of 1.2 eV. However, post-hoc GGA corrections to this result increased the barrier to 1.51 eV.

IV. STM OBSERVATIONS

STM pictures at low coverages have been taken in the temperature range 400–700 K. The features common to all these pictures are a background of clean dimer rows (grey) with some dark ''missing dimers,'' which may be dimer vacancies or monohydride dimers since the defect density was observed to increase after dosing with atomic hydrogen. These two can be distinguished at sample bias voltages above ± 2 V.[21] However, the electric field at these higher voltages has a large effect upon the single hydrogen atoms, sweeping areas clean. So as to avoid this problem, in this work the sample bias voltage was maintained at about −1 V, and at this voltage it was not possible to distinguish between the two. The brightest features are the bright white spots sitting asymmetrically on top of the silicon dimers, which indicate the presence of a hydrogen atom.[8] All these features may be seen in Fig. 1. The adsorbed hydrogen appears dark in the STM picture because the energy of the Si-H bond is about 2 eV below the Fermi level compared to the silicon σ-bond, which is at about −0.7 eV (Ref. 8) below the Fermi level; this difference produces a change in contrast equivalent to about an Å.[8,21] The white spot is due to the clean end of the silicon dimer, where there is a half-filled dangling bond, very close in energy to the Fermi level. It is very easy

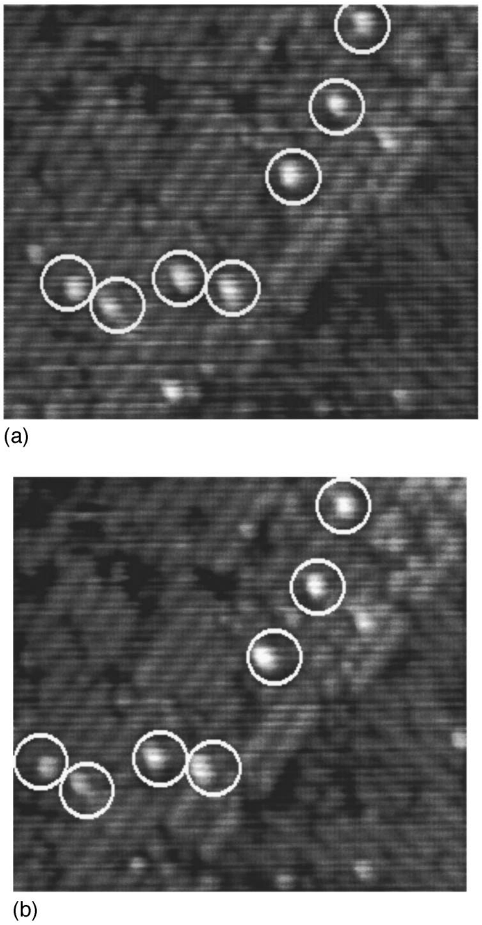

FIG. 1. STM pictures taken at 500 K, with imaging conditions of −1.3 V sample bias and 0.08 nA. The images are 14 nm wide. The grey rows are the silicon dimers, while the white dots mark the positions of the adsorbed hydrogen atoms, several of which are indicated with a white circle. There is a step edge running diagonally across the picture. (a) and (b) are separated by 15 min, during which time there has been no change in position of the hydrogen atoms.

to tunnel into or out of this bond, and it appears as a bright spot in both filled and empty states pictures. As the hydrogen may adsorb on either end of the dimer, the dangling bond may be in either of two symmetrically equivalent positions relative to the dimer row. In Fig. 1 these appear asymmetrical; as the apparent asymmetry varies from image to image, we believe that this asymmetry is due to the tip rather than surface.

The bright spot mentioned above is indicative of an adsorbate. However, as an STM cannot provide local chemical information directly, a series of control experiments were performed to check that the adsorbate was indeed hydrogen. The surface was imaged under different control conditions: without dosing; after the filament had been turned on, but without introducing any gas; and with gas, but without a cracking filament. Only when the gas was cracked by the filament, i.e., under the experimental, not the control, conditions, were any white dots seen. Thus these dots may be identified as the result of atomic hydrogen adsorption, rather than contaminants such as oxygen or water. Since we have used the minimum dose to give a suitable number of white dots on the surface, the likelihood that higher hydrides are forming is very small.

Pictures obtained at temperatures up to 500 K show very little change from picture to picture. Figures 1(a) and Fig. 1(b) were taken at 500 K and are separated by 15 min, in which time there has been no movement between pictures. However, at this temperature there are occasional changes between pictures; a white dot will sometimes appear or disappear from the picture. After a disappearance, the white dot is replaced by either a dark hole or a clean dimer. A dark hole is likely to be the result of two hydrogens pairing, while a clean dimer must be the result of desorption. There are usually a few appearances or disappearances of white dots in a sequence of pictures. It is possible that these events are the result of adsorption and/or desorption from the background pressure of hydrogen.

At higher temperatures, the dots start to move between pictures. They do not all move at a uniform speed; within the same data some dots remain stationary, while others have hopped long distances in a few seconds, so the motion of individual atoms cannot be followed. This behavior is shown in Fig. 2, which was taken at 600 K. The large distance that some atoms move may indicate that the hydrogen is not limited to single-dimer hops. As the temperature is raised, the proportion of hydrogens not moving between pictures drops, but even at very high temperatures, there are usually one or two atoms which remain stationary, which perhaps are pinned in some way. Above 600 K, features which we have called ‘‘smudges’’ appear (Fig. 3). These features are strings of white and darker lines running down dimer rows with random spacing between the lines, replacing the localized white dots imaged at lower temperatures. At 620 K, fuzzy dots coexisting with short smudges are imaged, while by 650 K virtually all the white dots have become smudged. By changing the temperature, the transition from localized dots to elongated smudges can be observed. Smudges have been previously observed in the case of silicon dimer diffusion on Si(001) by Schwartzentruber.[22]

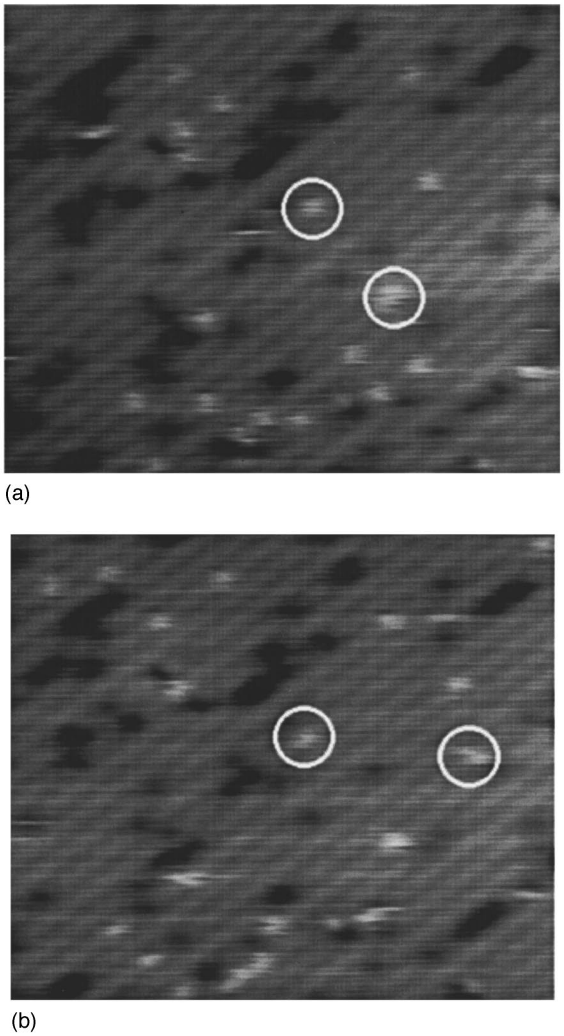

FIG. 2. STM pictures taken at 600 K, with imaging conditions of -1 V sample bias and 0.08 nA. The images are 20 nm wide. At this temperature, the white dots are a little fuzzy, which is the result of their motion during scanning. (a) and (b) are separated by 10 s, during which time the positions of some of the hydrogen atoms have changed dramatically, while others have barely moved. Two hydrogens are circled; one has apparently moved a long distance (many dimers) while the other has only moved a little (about two dimers).

The reason that smudges appear is because the hydrogen moves between linescans (i.e., about once every $\frac{1}{50}$th of a second). A dimer is sampled by about four tip linescans. If, after the tip has recorded the presence of a hydrogen as a white line, the atom hops before the tip returns to that dimer, then on the next scan the hydrogen will be absent and so a dark line will be recorded. Later, as the hydrogen hops along the dimer row, the tip may catch up with it again and another white line will be produced. Thus the image of a hydrogen atom will be broken up into a series of lines, which we have called smudges. To quantify the minimum hopping probability required for smudges, a primitive simulation was performed simulating the interaction of the slowly-moving tip and a random-walking hydrogen with a variable hopping probability. Smudges were produced in this simulation for hopping probabilities of greater than 0.3/scan line.

It is possible that the observed hopping may have been induced by the interactions between tip and sample inevi-

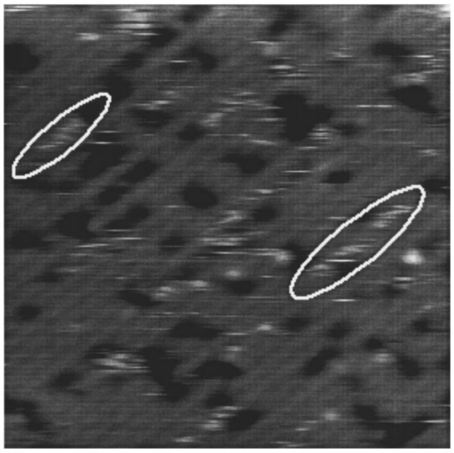

FIG. 3. STM picture taken at 640 K, with imaging conditions of -1 V sample bias and 0.08 nA. The image is 30 nm wide. The fuzzy white dots have broken up into elongated smudges, two of which are indicated with white ellipses. These smudges are the image of a hydrogen atom which is moving at or above the speed of the tip. Each scan line here takes $\frac{1}{25}$th of a second. Smudges begin to occur when the hopping probability in the time of one scan line is around 0.3.

table in STM. There is a very strong electric field between the tip and sample, which could locally increase the hopping probability. Although the tip spends only a small fraction of its time scanning a particular hydrogen atom, this could be enough to skew our results. To reduce the electric field and so minimize the interaction of the tip, low sample bias voltages ($\leqslant 1$ V) and low currents ($\leqslant 0.1$ nA) were used. Experimentally, it was found that the useful voltage limit was about 2 V, above which the area under the tip was swept clean of hydrogen, and the current limit was about 0.15 nA, above which hydrogen atoms were picked up by the tip and caused streaking of the picture. In similar experiments on a saturated surface, with the conditions for noninteraction described above, it was found that the same area of surface could be scanned repeatedly with no change in coverage, while at higher voltages significant tip-induced desorption occurred. It can be concluded, therefore, that the interaction is not significant under the imaging conditions used.

From the data, upper and lower limits can be put on the hopping probability over a range of temperatures. If the hydrogen is not moving around, then the hopping rate is less than one hopping event by one of the imaged atoms over the imaging time. When the hydrogen is observed moving around, the upper limit is the probability of motion during a scan line, while the lower limit is the probability of moving between pictures. For the smudges, the hopping probability during the period of one linescan is at least 0.3 (see above). Because of the exponential variation of mobility with activation energy, these approximate speed limits are sufficient to give a value for the barrier and have the advantage of being easily and accurately gathered from the data. When the hydrogen is observed moving around, an estimate could be made of the speed of motion by assuming ''random walk'' motion of the white dots between pictures. This, however, is more problematic to obtain, as the dots cannot be easily traced between pictures. Furthermore, this analysis assumes single length, independent hops, whereas the data suggest that multiple hops are occurring.

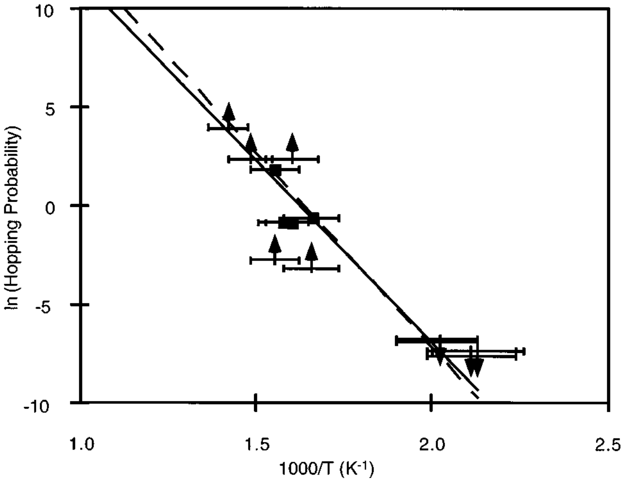

FIG. 4. An Arrhenius plot of the hopping probability against inverse temperature for the motion of single hydrogen atoms. Three different types of data point are shown; measured hopping probabilities and minima and maxima (indicated by arrows). Details are given in the text. The solid line is fitted to a preexponential factor of $10^{13}\ \mathrm{s}^{-1}$ giving an activation barrier of 1.68 eV. The dashed line is fitted to a preexponential factor of $10^{14}\ \mathrm{s}^{-1}$ giving an activation barrier of 1.80 eV. The error bars in hopping probability correspond to the variation in measured hopping rate from picture to picture within a sequence. The error bars in temperature correspond to an error of 30 K.

An Arrhenius plot of these data is shown in Fig. 4. The data points are shown with error bars; in the x direction, these represent an error of 30 K, while in the y direction they represent the variation between individual pictures in a sequence. Some of these data points represent maxima and minima; the maxima are indicated by arrows pointing down, the minima by arrows pointing up, and the measured hopping probabilities as squares. If an attempt frequency of $10^{13}\ \mathrm{s}^{-1}$ is assumed (which is a median figure for Si-H bond vibration frequencies in the literature,[23]) then the barrier is 1.68 eV. The solid line in Fig. 4 shows our best fit line to the data given this attempt frequency. Using an attempt frequency of 10^{14} the barrier is 1.80 eV (as shown by the dashed line in Fig. 4). Since the low-temperature data are maxima, and the high-temperature data are minima, $10^{13}\ \mathrm{s}^{-1}$ is the minimum attempt frequency consistent with the data. Furthermore, while the tip-sample interaction as discussed above is not significant, any such interaction can only increase the observed hopping rate, and thus decrease the observed barrier. Therefore, the value of 1.68 eV is a minimum.

V. COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

In agreement with Boland's observations,[8] a low coverage of hydrogen adsorbed at room temperature is found to be randomly distributed, and no pairing has occurred. This implies that the hydrogen is immobile at room temperature. Above 570 K, the hydrogen starts to become mobile, and by 640 K is moving as fast as or faster than the tip is scanning, so that ''smudges'' are formed. The experimental barrier is

1.68 ± 0.15 eV. Our tight-binding calculations predict a minimum energy barrier of 1.65 eV. It should be stressed that the tight-binding parametrization used[13] was fitted to data from the silane molecule, and not to any hydrogen diffusion data. Our LDA DFT calculations gave a barrier of 1.2 eV, comparable to the value of 1.3 eV obtained by Vittadini *et al.*[5] However, post-hoc GGA corrections increased the barrier to 1.51 eV. This change is due to the breakdown of LDA in the low electron density regime, which causes it to overbind at the midpoint and therefore underestimate the barrier. Application of GGA should give a better value for the binding energy at the midpoint, and hence a more accurate barrier. Both the tight-binding and GGA results are in good agreement with our experimental value, and with the value of 1.65 eV from the CI calculations corrected for substrate relaxation.[7] These experimental and theoretical results lend great weight to Widdra's conclusions that a mechanism such as the mobile delocalized state[9] must operate during chemisorption, as thermal diffusion cannot explain his observations of hydrogen pairing below room temperature.

VI. CONCLUSIONS

The motion of isolated hydrogen atoms along dimer rows has been followed in real time. There is no apparent movement at temperatures below 500 K. Above 640 K, the hydrogen is moving as fast as or faster than the tip scan speed. Motion across the dimer rows is rarely observed. From the speed of the motion, the activation barrier for intrarow diffusion has been measured to be 1.68 ± 0.15 eV, assuming an attempt frequency of 10^{13} s^{-1}. Gradient corrected LDA calculations have also been performed, and predict an activation barrier of 1.51 eV, consistent with the experimental results; previous calculations in which either gradient corrections or substrate relaxations were not included have been shown to be inadequate. Tight-binding calculations produced a respectably similar energy barrier, suggesting that with the parametrization used this may be the method of choice for larger scale calculations.

Our experimental and theoretical results are in good agreement with one another, and show that thermal diffusion cannot operate below 500 K, and that a mobile precursor mechanism may therefore be responsible for hydrogen pairing.

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*Electronic address: dave.bowler@materials. ox.ac.uk

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