

Low coverages of lithium on Si(001) studied with STM and ARUPS

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We have used scanning tunneling microscopy (STM), scanning tunneling spectroscopy, and synchrotron based angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) to study the initial stages of the adsorption of lithium onto the Si(001)- 2×1 surface. Our STM study shows that the half-missing dimer defects (*C* defects) act as sites for Li adsorption on this surface. Once these are occupied the Li adsorbs on top of the dimer atoms and forms small clusters, which stabilize the dimer buckling seen by the STM into areas of $c(4\times 2)$ symmetry. This is observed with ARUPS as a peak at the Fermi level, originating from partial occupation of an empty surface band associated with the $c(4\times 2)$ reconstruction. On *p*-type Si substrates, STM shows that small amounts of Li cause further dramatic changes to the electronic structure of the surface. We observe negative differential conductance (NDC) on both Li sites and clean Si dimers, as well as digital switching in the tunnel current over the Li sites. We propose that this trapping noise is caused by electrons emptying and filling thermally activated traps close to the Fermi level and that the NDC has its origin in coulombic repulsion by occupied traps on the surface.

INTRODUCTION

Adsorption of alkali metals (AM's) onto semiconductor surfaces has been the subject of extensive studies in the past decade.¹ Because of their relatively simple electronic structure, the alkali metals are used as model systems for adsorption studies, providing information about, for example, metal-semiconductor contacts and metallization processes. One of the most investigated surfaces in this context is the technologically important Si(001) surface, but, despite a large number of investigations, studies involving the lightest of the alkali metals, lithium are rare.²⁻¹¹ Recent studies with low-energy electron diffraction (LEED) (Refs. 8 and 11) and photoemission,⁸ have shown that submonolayer coverages of Li have a dramatic effect on the surface reconstruction on a long length scale.

With a scanning tunneling microscope (STM), even very small amounts of an adsorbate are accessible for studies, which is not the case for most surface science techniques. The STM study presented here is concentrated on the very initial stages of the adsorption of Li on Si(001), addressing the question whether the Li tends to sit on defects and step edges or on top of the dimer atoms.⁶ Our results show that the half-missing dimer defect (*C*-type defect) acts as the first adsorption site. Once the *C*-type defects are occupied, Li adsorbs on top of the dimer atoms, in agreement with earlier STM studies,^{6,7} and forms small clusters.

The Li atoms and clusters stabilize the buckling of the dimers, resulting in a local $c(4\times 2)$ periodicity. This leads to the occupation at the Fermi level of an empty surface state, associated with the $c(4\times 2)$ reconstruction, which we observed with angle-resolved ultraviolet photoelectron spectroscopy (ARUPS).

EXPERIMENTAL DETAILS

The STM experiments were performed with a UHV-scanning tunneling microscope¹² operated at a base pressure

of $<3\times 10^{-11}$ mbar. The UHV chamber is equipped with LEED and Auger-electron spectroscopy systems¹³ for determination of surface order and cleanliness. The STM has, in addition to ordinary constant current topographs, an operational mode for *I-V* measurements using the current imaging tunneling spectroscopy (CITS) method. We normally take the average over spectra acquired at locations with similar topographic characters, within the same measurement, in order to reduce noise and spurious artifacts in the tunneling spectra. The photoemission measurements were performed at beamline 52 of the MAX-Lab synchrotron radiation facility, Lund University, Sweden, which is equipped with a 1-m normal-incidence monochromator working in the photon energy range 5–30 eV, and a Vacuum Generators ADES 500 spectrometer.

The substrates used for the experiments were cut from (001)-oriented silicon wafers.¹⁴ We have used different methods of preparation before transfer into vacuum: (1) degreasing in methanol, (2) degreasing and etching in HF-H₂O solution, and (3) a wet etching treatment described by Ishizaka and Shiraki.¹⁵ Pretreated samples were then transferred into the UHV chamber, outgassed at 300–400 °C for 12 h and, finally, repeatedly flashed at 1150–1200 °C for 5–10 s by direct current resistive heating until a well-ordered and clean surface was obtained. After each flash the temperature was decreased rapidly to 800 °C, and finally the sample was cooled to room temperature over a period of about 5 min. No variance in the final result due to different pretreatments was discerned. Both *p*-type Si(001) (B, 0.02–0.03 Ω cm) and *n*-type Si(001) (P, 0.2–0.4 Ω cm) have been used for the measurements.

The evaporation of Li was performed with a well-outgassed getter source (SAES Getters S.p.A.). During the evaporation the pressure in the chamber never exceeded 3×10^{-10} mbar. The coverage was estimated by measurement of the change in work function determined by secondary electron cutoffs in the photoemission experiment, and by inspection of the STM topographs in the STM experiment.

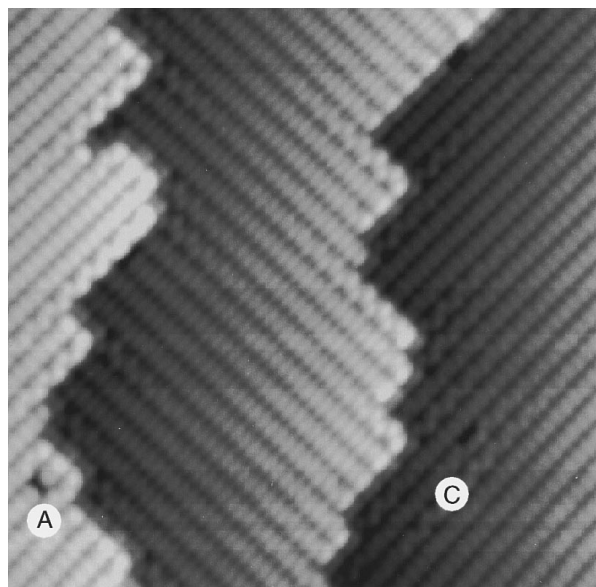


FIG. 1. Filled states topograph of the Si(001)-2 \times 1-reconstructed surface ($V_s = -1.8$ V, $I_t = 0.3$ nA, 20×20 nm 2). Denoted in the figure are the defect types A (missing dimer defect) and C (half-missing dimers).

RESULTS AND DISCUSSION

Early STM studies of the clean Si(001)-2 \times 1-reconstructed surface¹⁶⁻¹⁸ showed the presence of characteristic defects on the surface, denoted A, B, and C, where the type-A and -B defects are single- and double-dimer vacancy defects, respectively. In this study we turn our attention to the type-C defect, a vacancy type where one of the dimer

atoms appears to be missing, resulting in the observation of protrusions in empty states topographs. The metallic character of the C defect was established by *I-V* measurements made by Hamers and Köhler,¹⁸ showing drastic changes between the tunneling spectra acquired on and close to the C defect. Figure 1 shows a filled-states topograph of a clean Si(001)-2 \times 1-reconstructed surface with defect types denoted as mentioned above. Patches of stabilized asymmetric dimers in the vicinity of defects and outside step corners are present, as previous reports have shown.¹⁸

The STM measurements presented here of the Li-adsorbed Si(001) surface is concentrated to a coverage of about 0.005 ML (1 ML here is defined as the Si-atom density of a full monolayer, i.e., 6.8×10^{14} atoms/cm 2). Applying a negative tip bias with respect to the sample immediately resulted in a transfer of Li atoms from the sample to the tip and the loss of clean tunneling conditions. This behavior has been reported for K/Si(001),¹⁹ and is very likely due to the electropositive character of Li. Therefore only topographs and tunneling spectra of the filled states are possible.

Figure 2(a) shows a typical filled-states topograph of an Li-adsorbed Si(001) surface. The type-A defect and its derivative multiple-vacancy defects are still present, but the type-C defects seems to have disappeared. A careful inspection shows that the C defects are not missing, but they now appear as protrusions in the topograph, indicating that they now have a higher density of filled states. We interpret this to be due to Li occupying the defect. Different types of Li clusters and a second adsorption site on top of the dimer atoms (as proposed in Ref. 6) are clearly observed in Fig. 2(a). An enlarged view of two types of small clusters, denoted K_1 and K_2 , is shown in Fig. 2(b). Taking into account the metallic radius of Li (1.52 Å), these two clusters are likely to be two successive stages of Li clusters, with K_2 having one more Li atom than K_1 . A highly buckled dimer is seen next to the smallest cluster K_1 , which is incorporated into the larger cluster, K_2 . Hasegawa *et al.*⁶ reported that Li

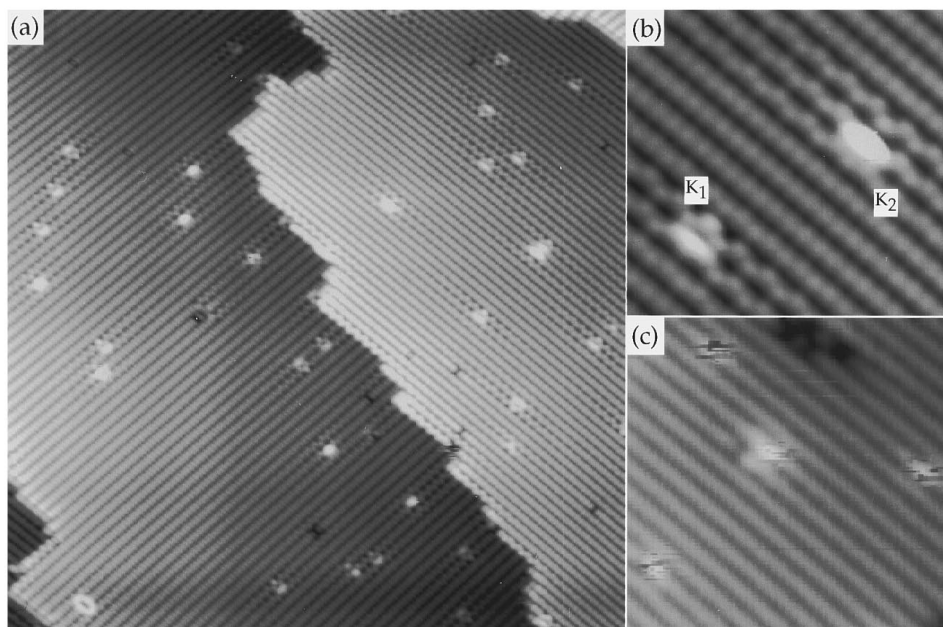


FIG. 2. STM topograph of Si(001)-2 \times 1 with a coverage of 0.005 ML of Li. (a) $V_s = -1.5$ V, $I_t = 0.2$ nA, 47×47 nm 2 , *n* type. (b) $V_s = -1.5$ V, $I_t = 0.25$ nA, 8×7 nm 2 , *n* type. (c) $V_s = -1.2$ V, $I_t = 0.1$ nA, 11×11 nm 2 , *p* type.

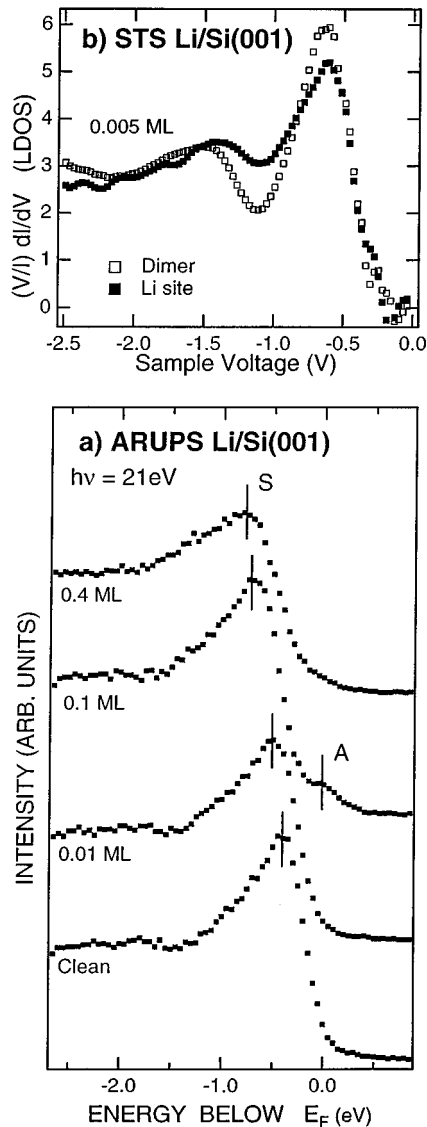


FIG. 3. (a) Normal-emission ARUPS spectra measured on the Li-deposited Si(001)- 2×1 surface for increasing Li coverage. (b) Normalized conductivity curves on the Li-exposed Si(001) surface at a coverage of 0.005 ML. The dimer spectra are averaged over 542 individual IV curves, and the lithium spectra are averaged over 135 individual IV curves.

stabilizes the buckling of the dimers into small patches of $c(4\times 2)$ and $p(2\times 2)$ symmetries around the Li clusters, which is also observed here. On p -type samples topographs tended to have much lower resolution than on n -type samples, and a characteristic trapping noise could be observed when the tip was over the Li sites, as shown in Fig. 2(c). This will be discussed in greater depth below.

Figure 3(a) shows ARUPS normal-emission spectra of the Si(001) valence band for increasing Li deposition. Here we have defined the coverage corresponding to a work-function change of $\Delta\Phi = -1.8$ eV as 1 ML, following earlier photoemission studies.³⁻⁵ The peak denoted S corresponds to the filled dangling-bond state. This peak shifted downward in energy and became broader with increasing coverage, as reported earlier.⁴ In addition, an extra peak, denoted A in Fig. 3(a), became visible at the Fermi level on the Li-adsorbed

surface. The intensity of peak A reached a maximum at a coverage of 0.1 ML, and then decreased with further Li deposition, and could not be observed for coverages >0.4 ML. It should be emphasized that peak A was observed in the same coverage regime on both p - and n -type samples. Our ARUPS measurements revealed that the A peak is highly localized (to within a few degrees of normal emission) around the $\bar{\Gamma}$ point in k_{\parallel} space, which implies that this state is somewhat delocalized in real space.

Figure 3(b) shows tunneling spectroscopy from a Li site and a Si dimer at a Li coverage of 0.005 ML. Both spectra are dominated by a peak at 0.6 V, which corresponds to the π -bonding dimer state S seen in ARUPS. However, there is a clear difference between the spectra at voltages between -1.0 and -1.5 V, where the Li site has a higher local density of states. We would not expect to observe the difference in the ARUPS spectra because the extra intensity only occurs at the Li adsorption site, and the Li concentration is too low.

Analogous observations were made earlier^{20,21} on clean, highly n -doped Si(001), where a state appeared at the Fermi level as a result of excess electrons on the surface that partially filled an empty surface state. Similarly, an inverse photoemission study²² showed that existence of two dispersive empty surface bands in the band gap, one of which had a minimum close to the Fermi level at $\bar{\Gamma}$. It was argued that this state was associated with areas of correlated, asymmetric dimers which formed a $c(4\times 2)$ reconstruction. Calculations of this Si(001)- $c(4\times 2)$ structure^{23,24} do indeed show a minimum in the empty surface-state band at the $\bar{\Gamma}$ point. On the other hand, in a STM study¹⁸ it was suggested that the peak in Refs. 20 and 21 originates directly from states localized on the C defects.

Our results suggest that a combination of the two interpretations is appropriate. The C defects induce or stabilize buckling of the dimers around them, and thus create a patch of $c(4\times 2)$ -reconstructed Si. All the Li adsorption sites and clusters have a similar effect, although their influence extends over a larger area, as would be expected for an adsorbate which actively injects charge into the surface. We suggest that peak A appears when the Li density is sufficiently high that a substantial proportion of the surface is $c(4\times 2)$ reconstructed, and sufficient charge has been transferred from the Li atoms to the substrate. If this is the case, similar effects would be expected upon adsorption of low concentrations of other alkali metals, as has indeed been observed in studies of K/Si(001) (Refs. 25 and 26) and Cs/Si(001).²⁷

We therefore interpret peak A as originating from a stabilization and partial occupation of an empty surface band by the Li. Unfortunately it is not possible to say how much the appearance of the $c(4\times 2)$ state is due to charge injection from the alkali metal, and how much it is due to localized stresses around the adsorption site, but a satisfactory theoretical explanation should consider both effects.

The effects discussed above were observed on both n and p -type substrates. However, on p -type silicon, further interesting electronic effects were observed in the STM experiments. This includes the trapping noise seen over the Li sites in Fig. 2(c), as well as negative differential conductance seen in tunneling spectra taken on both the Li sites and clean Si dimers.

Figure 4 shows differential conductance curves (dI/dV)

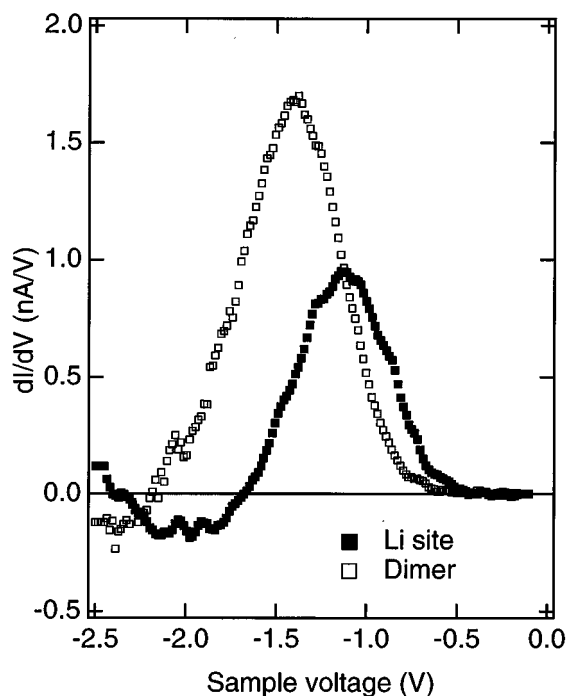


FIG. 4. Differential conductivity curves (dI/dV) acquired on Li-Si(001)- 2×1 . The dimer and lithium spectra are averaged over 92 and 72 individual I - V 's, respectively.

acquired at different positions on the p -type surface. The region of negative differential conductance (NDC), centered at -2.0 V, is very clear for the spectrum taken with the tip directly over a Li site. However, the second curve in Fig. 4 shows that a weak region of NDC also occurs when tunneling out of a Si dimer. Such NDC was observed for all the dimers on the p -type surface, even those outside the patch of asymmetric dimers surrounding the Li site.

Earlier STM studies have reported NDC for systems such as oxidized silicon,²⁸ boron-Si(111),^{29,30} and germanium-Si(001),³¹ where it was either explained in terms of the filling of electron traps by tunneling electrons²⁸ or resonant tunneling between localized states on the tip and surface.²⁹⁻³¹

We believe that the NDC observed here cannot be explained by tunneling between localized states. Because the NDC is observed when the tip is over a silicon dimer, any explanation involving localized states must explain why we do not observe NDC when using the same tip and same silicon sample before any Li is deposited. Also, we have observed NDC using several different tips and several different samples, so an explanation involving a particular tip geometry, as has been proposed to explain the B-Si(111) results,³² also seems unlikely.

Our results are similar to those obtained on oxidized silicon, where both NDC and trapping noise have been observed when the STM tip is positioned above a trapping site in the oxide. In that case the trapping noise results when near-Fermi level traps are filled by thermally excited electrons, whereas the NDC is associated with the filling of different traps, 1 eV or more away from the Fermi level, by electrons tunneling from the tip.²⁸ In contrast, on this surface both effects seem to be caused by a single, long lifetime trap

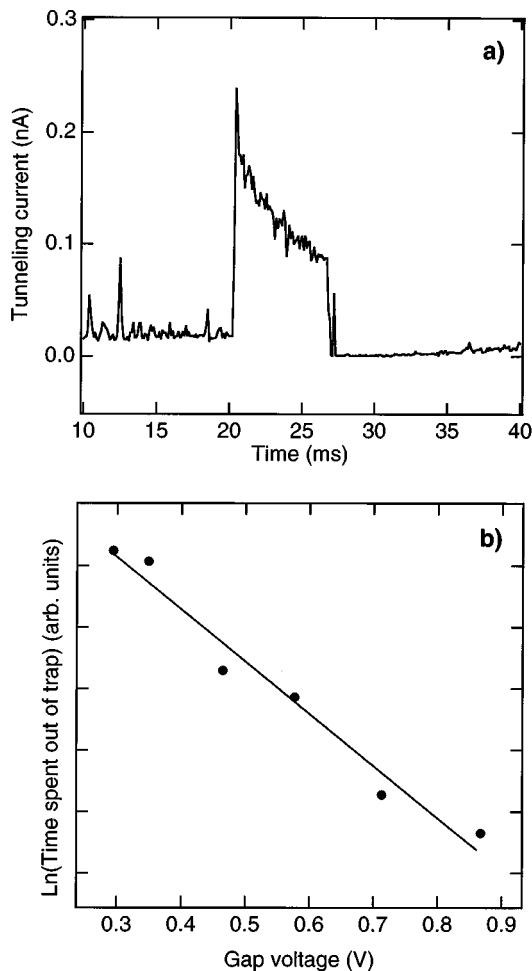


FIG. 5. (a) Current trace for a typical trapping event with the tip positioned above a Li site. (b) Average time analysis for the time spent out of a trap vs the applied gap voltage. The straight line is a least-squares fit to a Poisson distribution.

localized on the Li adsorption site.

When the STM tip is over a Li site, the trapping noise seen in Fig. 2(c) occurs. If the tip is held stationary the tunnel current is seen to jump suddenly, as shown in Fig. 5(a). Both STM of oxide traps^{33,34} and macroscopic investigations of metal-oxide-semiconductor field-effect transistor (MOSFET) devices³⁵ show a similar switching, where the current flow in the vicinity of the trap is reduced when the trap is filled, as the occupying electron repels nearby conduction electrons.

In the case of thermally activated oxide traps close to the Fermi level, the probability of the trap being occupied could be varied by applying an electric field and thus changing the potential of the trap with respect to the surface Fermi level. In the STM this results in a change in the average time taken to fill and empty the trap, and the traps' occupation statistics follow a Poisson distribution as a function of tip bias.³⁴ In Fig. 5(b) we plot the logarithm of the mean time that a typical Li trap remains empty as a function of tip bias. The data fit a straight line well, which is good evidence of thermal activation of traps whose energy with respect to the Fermi level varies with the electric field in the tunnel gap.

Unfortunately, the precise mechanism by which the trap

energy changes is not clear. It is possible that a state associated with the Li atom experiences a Stark shift with respect to the surface Fermi level, or that tip-induced band bending moves all the surface states with respect to the bulk Fermi level. Evidence that the second mechanism might occur is provided by surface photovoltage measurements on the clean surface,³⁶ where tip-induced band bending was clearly demonstrated.

A more complete analysis of the trapping noise as in Refs. 33 and 34 would be welcome, but the much longer trap lifetimes make this difficult. If the STM feedback loop is left on while the current is measured, it changes the distance between the tip and the surface in reaction to the jumps in the current [which explains the obvious slow variation seen in Fig. 5(a)], and therefore affects the electric field on the trap. On the other hand, if the loop is frozen for long enough to take statistically significant data, a tip crash is almost inevitable.

Nevertheless, from measurements of the NDC and the trapping analysis the following interpretation arises. The adsorbed Li creates a trapping state close to the surface Fermi level. As the tip bias varies, the occupation statistics of the trap also change. *I-V* spectra represent the average tunnel current and therefore show a region of NDC where the trap becomes progressively more likely to be filled. Because the trapping state is physically on the surface, it has a direct effect on the surrounding surface states, and so the filled trap can block current even at some distance from the trapping site, which is why we observe NDC over the whole surface. Finally, we do not observe any of these effects on the *n*-type

substrate, because electrons from the bulk ensure that the trapping state is permanently occupied.

CONCLUSION

In this study of the lithium-adsorbed Si(001)-2×1 surface, we report that Li has a preferred initial adsorption site on the half-missing dimer defects. With increasing deposition the Li adsorbs on top of the dimer atoms and forms small clusters. The Li stabilizes the apparent buckling of the dimers, which is observed with STM as small areas of *c*(4×2) symmetry surrounding the Li sites. In ARUPS this is observed as a peak at the Fermi level due to the partial occupation of a surface band associated with the *c*(4×2) reconstruction. On *p*-type silicon we observed, with STM, negative differential conductance (NDC) in our *I-V* measurements that is present on both the Li sites and the clean Si dimers, as well as trapping noise in the tunnel current over Li sites. We find evidence that the noise is caused by electron traps localized to the Li adsorption site, and having energies close to the Fermi level which are thermally activated. We propose that these Li-induced traps give rise to the NDC that is seen in the scanning tunneling spectroscopy (STS). In general we have shown that even very small amounts of Li on Si(001) have drastic effects on the electronic structure of the surface.

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