УДК 537.534.8

HYDROGEN INTERACTION WITH VACANCY DEFECT ON SI(100) SURFACE

A.S. Yanovsky, A.P. Kotlyarov

1. INTRODUCTION

A classical example of a heterogeneous chemical reaction is recombinative desorption of two atoms from well-defined surfaces. In the elementary case the process involves a breaking of two adatom-surface bonds and formation of diatomic molecule with single new atom-atom bond. However, such a trivial description of the process can neglect the role of a solid surface. Effects such as reconstruction of a surface, the local modification of electronic states or even the formation or breaking of chemical bonds between surface atoms can essentially influence energetics and dynamics of reactions and complicate the mentioned above elementary model. In this connection a "hydrogen -Si(100)" system is an excellent example.

The hydrogen is an elementary adsorbate and at the same time plays the important technological role. The clean Si (100) - (2X1) surface was a subject of numerous researches and at the present time its geometric and electronic structure is well known, therefore with a large degree of reliability it is possible to state, that well-ordered Si (100) surface is characterized as a superstructure with rows of interacting asymmetric buckled dimers [1-6]. Such relative determinancy of physical properties of a "hydrogen - Si (100)" system makes it an convenient model object.

In the present work on the basis of the early experimental works [7] by means of MNDO semiempirical method a vacancy defect on a Si(100) surface and its interaction with hydrogen have been simulated.

II. CALCULATION PROCEDURE

The calculations were carried out within the framework of a semiempirical MNDO method for a clusters Si_{33} on the computer Acer 7000.

We chose cluster size and calculation method to have a possibility to simulate the influence of reconstruction, relaxation and surface coverage on adsorption and desorption processes in accordance with available computational resources. The initial cluster Si_{33} was constructed from five fragments Si_9, containing two atoms on a surface, four atoms of the first, two of the second and one of the third subsurface layer. Dangling bonds in the bulk of solid were saturated by hydrogen atoms (model of univalent pseudo-atoms).

Geometry of an initial cluster was optimized with symmetry restriction C_{2V} for Si atoms of each fragment. The hydrogen atoms were free optimized. Dangling bonds at eight surface atoms on this stage were saturated by five groups SiH_2.

Then, at a fixed hydrogen positions and full geometry optimization for Si atoms of all subsurface layers, ordered 2x4 surface was simulated. The result of calculations for clean ordered surface are three rows of buckled dimers (see fig.1).

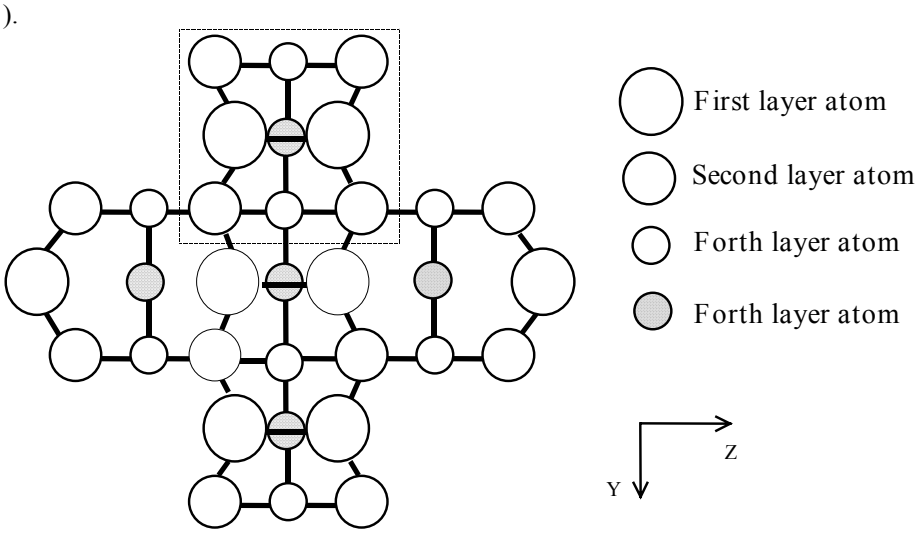

Fig.1 2X2 reconstructed surface. The dotted line indicates a basic Si_9 fragment.

III. RESULTS AND DISCUSSION

The modelling of the vacancy defect on a Si (100) surface was performed by removing of one dimer atoms from the central fragment. Then we search for equilibrium geometric configurations by varying of remained dimer atom position within the first and second atomic layer in direction normal to the surface and along the surface within central dimer row.

A ground state of the defect Fig.2(a) has C_2 symmetry. First quasiequilibrium state Fig.2(b) is 5 kcal/mol higher and has C_0 symmetry, it contains remained dimer atom located above fourth layer central fragment Si atom.

The next is the state (9 kcal/mol above ground state) with a similar symmetry Fig.2(c) and remained dimer atom position is close to ideal unreconstructed Si(100) surface position. The valent electron orbitals of defect dimer atom in these three states are in sp-hybridization. In contrast to Si bulk vacancy research [8], these configurations have no "long" silicon bond. The reasoning is higher mobility of Si atoms at the surface than in the bulk of solid. Thus two second layer atoms each with the single dangling bond are in sp^2-hybridized state and have shorter back bonds lengths. Such electron density redistribution cause charge transfer to these atoms ~0,4*e* from the dimers in adjacent rows. These processes lead to increasing of neighbour dimers asymmetry.

Only the third quasiequilibrium state (10 kcal/mol above ground state) has the long bond between second layer Si atoms see fig.2(d). This bond length is 2,8A against the 3,7A [8], that accounted for the nature of surface defects, i.e. a high mobility of the nearest neighbour atoms in comparison with the bulk. Also, M.A.Roberson and S.K. Estreicher [8] have optimized nearest neighbour atoms only, while in our treatment all Si atoms in the cluster Si_{32} were optimized. In this vacancy configuration dimer atom with sp^3-hybridized orbitals located between the second and third atomic layer. It forms one additional weak bond with nearest third layer atom (shown by a dotted line on Fig.2(d)).

Sequential dangling bond saturation by atomic hydrogen in any of these configurations leads to formation of a one uniform state. Note, that at first hydrogen saturates dangling bonds of the remained dimer atom, and then dangling bonds of two second layer atoms. We have found adsorption barrier 6 kcal/mol (for a configuration (d) the adsorption barrier is ~2 times higher, because of energy losses for long Si-Si bond breaking).

In early works [5, 7, 9] two alternate mechanisms of hydrogen desorption from SiH_2 complexes were discussed:

Desorption from hydrogen saturated surface starts with breaking of one Si-H bond on each surface complex SiH_2, accompanied by dimerization of adjacent Si atoms by means of formed dangling bonds. As a result each surface atom is connected only with one chemisorbed H atom. I.e., in such model desorption from dihydride phase passes through the stage of monohydride formation [5, 7, 9];

Desorption by simultaneous breaking of two Si-H bonds at the same surface Si atom.

In [7, 9] we have established, that desorption from overequilibrium dihydride centers on preliminary ion bombarded surface follows the second mechanism, both for Si(111) and Si(100) surfaces. Obviously, such a model is proved to be correct for all two dangling bonds centers which are structural defects of “ideal” Si surfaces. Thus, it will be interesting to perform study of hydrogen desorption from "defect" surface adsorption center.

During the study of desorption process from a hydrogen saturated defect configuration it was established, that the desorption starts with decomposition of SiH_2 complexes on side Si_9 fragments, and follows the first mechanism, described above. Then hydrogen desorbs almost simultaneously from monohydride phase of side fragments dimers and from defect complex SiH_2 (desorption barrier ~58 kcal/mol) of central fragment. Desorption from defect complex involves only rupture of two Si-H bonds and H_2 molecule formation; no surface reconstruction or formation of new surface bonds is observed and this is the reason of comparatively high desorption barrier. At last hydrogen desorbs from monohydride phase of two second layer atoms. A final state of the defect cluster after complete hydrogen desorption is a state shown on Fig. 2(a). According to this data it is clear that a vacancy - hydrogen complex on a solid surface is more stable, than Si-H or SiH_2 complexes on an ordered surface.

IV. CONCLUSIONS

The research of a structure and adsorption properties of vacancy defect on a Si(100) surface have shown, that the desorption reaction from lonely dihydride center, formed in the defect region during interaction with hydrogen, looks like $SiH_2 \rightarrow Si+H_2$. There is no surface reconctruction during this reaction and desorption barrier is rather high (~58 kcal/mol), which almost coincides with the value of a desorption barrier from monohydride on an ordered Si(100)-2xl surface.

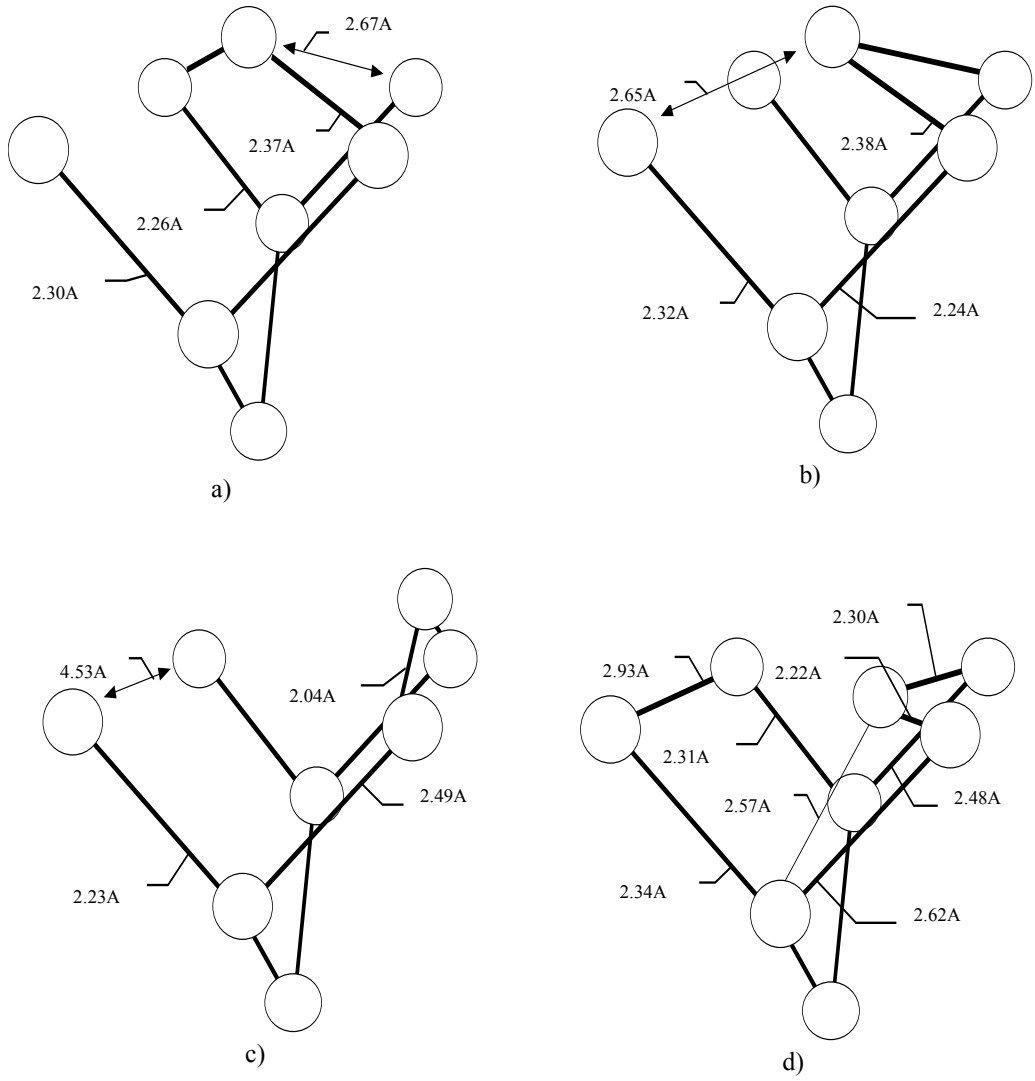

Fig.2. Vacancy defect configurations on Si(100) surface:
a)-a ground state;
b), c) and d) - first, second and third quasiequilibrium states.

REFERENCES

[1] W.Monch, Surf. Sci. 86, 672 (1979).

[2] W.S.Verwoerd, Surf. Sci. 99, 581 (1980).

[3] W.S.Verwoerd, Surf. Sci. 108, 153(1981)

[4] E.G.McRae, Surf. Sci. 124, 106 (1983).

[5] H.Froitzheim, U.Kohler, H.Lammering, Surf. Sci. 149, 537 (1985).

[6] T.Tabata, T.Aruga, Y.Murata, Surf. Sci. 179, L63 (1987).

[7] A.Yanovsky, M.Gerchikov, A.Panesh, Poverkhnost(USSR) 8, 5 (1989).

[8] M.A.Roberson, S.K.Estreicher, Phys. Rev. B 49, 17040 (1994).

[9] A.Yanovsky, M.Gerchikov, A.Panesh, A.Simonov, RAS USSR 295, 153 (1987).