Modeling Of Hydrogen Weight Storage Capacity In Solid Porous Silicon
Xiaozhong Song 1,a, Jie Wu 2,b

1Mechanical engineering department, Wright state university, Dayton, OH 45435, USA
2Fujian provincial light industry equipment installation engineering limited company, Fuzhou, Fujian 350003, P.R. of China
axzhsong@yahoo.com, b13906929716@139.com

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Abstract. Silicon-hydrogen crystalline models are proposed to estimate theoretical hydrogen storage capacity in porous silicon media with nanostructure features like cubic nodules, columnar forests and thin wall honeycomb like networks. To simulate these nanostructure features and their hydrogen storage capacities, three basic crystalline types (cubic, column and plate) have been developed as building blocks for constructing H-Si weight storage models under the assumption that hydrogen is chemically bonded to available surface silicon atoms. Using these models, the hydrogen weight storage capacity for all feature dimensions from unit to infinitely long can be estimated. According to these theoretical models, the best nanostructure for hydrogen storage is cubic nodule, columnar forest and thin wall network in that order. They have weight storage capacity limits of 5.77%, 5.21% and 2.78% respectively for infinitely large feature dimensions.

Introduction
The shortage of fossil energy will become more and more serious in the future as a result of expanded global economic development and the fact that the fossil resource is limited on the planet. On the other hand, the massive use of fossil energy causes many environmental problems, such as greenhouse effect, chemical pollutions and so on. All these issues push hydrogen fuel cell research a high priority around the world. One of the main challenges to a widespread use of hydrogen fuel cells is the development of a secure, compact, lightweight and economic hydrogen storage system. Of special interest among the existing hydrogen storage methods is the solid-state approach because it possesses significant advantages over others in safety.

In the solid-state storage domain the metal hydride is currently the leading candidate [1]. But it faces big challenges in its low weight storage capacity, $W_t$, which is defined as the ratio of hosted hydrogen weight to the host material weight plus hydrogen weight. Typically the hydrogen storage capability by weight is about 1.5-2.0% in current commercial grade metal hydrides. Clearly it is not competitive yet with the hydrogen storage methods either in gas or liquid state.

The mechanism for the current hydrogen storage method with metal hydrides is known as volumetric storage. Hydrogen absorption and desorption are accomplished by chemical reactions [2-4]. The current approaches to weight storage capacity estimate are almost exclusively based on experimental trials. Since the metal hydride is a complex chemical compound, it is difficult to establish a general quantitative theory or model for a volumetric storage capacity calculation. Besides metal hydrides, other methods using the enormous surface area in nano-scale media for hydrogen storage have also been proposed and studied. The most interesting ones are using carbon nanostructures and nanotubes. Simulation and experimental studies had indicated that it can get as higher as 5-10% $W_t$ storage capacity [5-8]. But based on the known techniques, it is very difficult to make nanotubes in commercial grade with hydrogen storage capacity anywhere near the 5-10% mark in recent. Silicon’s properties for hydrogen adsorption and desorption on surface were well known in semiconductor and photo-electronic industry [9-11]. So, porous silicon material recently was also proposed for hydrogen storage [12]. A very recent article has reported an optimal etching strategy to make the nanoporous microstructure in lab conditions [13]. Based on authors’ best
knowledge, all these studies are based on experimental studies to determine the \( W_t \% \) storage capacity. Then the questions are: What is its \( W_t \% \) storage limit? And which type of nanostructure has the best storage capacity?

A predictive hydrogen storage model will help for answering these questions. It will help devise new nanostructure morphology and production strategy, etching methods, process optimization and evaluation of test results without resorting to exhaustive experiments. With this in mind, basic silicon-hydrogen crystalline models are proposed to simulate silicon nanostructure for hydrogen storage. Based on different hydrogen bonding characteristics for internal and surface atoms, H-Si weight storage models for cubic, column and plate type nanostructures are established under the assumption that hydrogen is chemically bonded with silicon atoms. Using these models, hydrogen weight storage capacity limit was estimated for each case. Realistic nanostructure of porous silicon for hydrogen storage may be constructed based on these cubic, column and plate type basic building bricks. They have the theoretically hydrogen weight storage capacity limits of 5.77\%, 5.21\% and 2.78\%, respectively.

**Silicon crystalline and surface bonding to hydrogen**

The silicon microstructure of a crystalline material is known as a face center diamond cubic. Figure 1 shows its crystalline structure.

For single crystalline silicon, it is the smallest basic repeating solid unit for the bulk material. Each face center diamond cubic’s side dimension is 0.543 nm [14]. In the following study, it is used as the basis to construct other types of nanostructures for hydrogen storage capacity estimation. Each silicon atom has 4 electrons in its outer orbits, which may catch 4 other electrons to make itself a stable atomic state. For those atoms inside a regular crystalline lattice structure, they will bond with 4 neighboring atoms to form four co-valences and share their electrons. But for the atoms on the surface, they do not have symmetrical neighboring atoms to share their electrons. They have some extra free valences that are chemically active. When those atoms take on different positions in a unit diamond cubic crystalline microstructure, they will show up with different bonding potentials. In hydrogen storage cases, the storage mechanism is the interaction of these surface silicon atoms with available hydrogen atoms in the vicinity. How many hydrogen atoms can be bonded to the surface silicon atoms are determined based on the number of silicon atoms on the surface and how many free valences each silicon atoms has. If the exposed surface takes on \{100\} family plane orientations, each atom on that surface plane can have two free dangling valences to bond with hydrogen atoms. Figure 2 shows this situation. It can be seen in Figure 2, for each unit \{100\} surface there are three silicon atoms available to combine with six hydrogen atoms. Figure 2 also shows the hydrogen bonding conditions when the silicon atom takes on the
{110} and {111} family plane orientations. Each silicon atom on these planes only needs one hydrogen atom to turn itself into a stable state. Comparing with those cases, it can be shown that each silicon atom on {100} surface can catch two hydrogen atoms. On {110} and {111} surfaces each silicon atom only has one free valence to mate with one hydrogen atom. So among those orientation surfaces the {100} surface has the highest surface storage capacity. In modeling the limit hydrogen storage capacity in solid state, only the {100} family plane is considered.

Figure 2. Different silicon orientation surface hydrogen bonding condition: (a) {100} surface case, (b) {110} surface case, (c) {111} surface case.

**Modeling of porous silicon nanostructure and its hydrogen weight storage capacity**

Porous silicon is the silicon etched with many micro- or nano-scale holes all over its surface and volume. From the viewpoint of maximizing hydrogen storage, it should have as large surface area as possible. Now with an optimized etching process, it is possible to make the porous silicon with less than 10% of the material in initial silicon bulk and the rest of it will be voids in the form of micro- or nano-scale holes [13]. But compared with the unit diamond cubic, which is only $0.543\,nm$ in size, the nanoporous silicon with typical dimensions in the order of 2 to 5 nanometer can still be considered at least locally as crystalline in its microstructure to lower its energy state. It can be featured like nanostructure cubic nodules, columnar forests and thin wall honeycomb like networks as shown in Figure 3 and it could be further modeled as three basic forms of crystalline clusters.

It is assumed that the smallest storage unit is the diamond cubic, or cubic as shown in Figure 1. Consider this cubic as a stand-alone hydrogen storage unit; it has six face center atoms and four corner atoms at the top and bottom corners in diagonally opposed positions. Each face center atom has two valences used for bonding it with other atoms inside the cubic to form the standard diamond cubic lattice pattern. They have two free valences for bonding with hydrogen from outside. The atoms at the corner only have one valence to bind themselves with internal atoms, thus it has three free valences to bond with hydrogen atoms. Figure 4(a) shows this cubic model with hydrogen atoms illustrated as smaller black balls.

Figure 3. Modeling of Solid State Porous Silicon Nanostructures.
From this cubic storage model, it is known that there are 14 silicon atoms, and 24 hydrogen atoms chemically bonded to the surface and corner silicon atoms. Its weight hydrogen storage capacity can be obtained from following equation:

\[
W_t = \frac{n_h w_h}{n_s w_s + n_h w_h} = \frac{24 (1)}{14 (28) + 24 (1)} = 0.0577 = 5.77 \%
\]  

(1)

Where

- \(n_h\) = number of hydrogen atoms
- \(w_h\) = hydrogen atomic weight
- \(n_s\) = number of silicon atoms
- \(w_s\) = silicon atomic weight

Since the silicon atoms at the corner has only one valence to bond with other silicon atoms, this bond is weaker than the silicon atoms that have at least two bonds. When the external energy strikes this silicon-hydrogen cubic to release hydrogen it is possible that not only the hydrogen, but also the corner silicon atoms may be released. To release a silicon-to-silicon bond, it needs 226kJ/mole per bond while to dissociate the hydrogen-to-silicon bond, it needs 323kJ/mole per bond [15]. The latter is higher than the former so hydrogen would not release unless for whatever reason the hydrogen-to-silicon bonds gets more energy than the silicon-to-silicon bond. The cubic model in Figure 4(b) illustrates a case when the four corner silicon atoms are replaced by four hydrogen atoms after hydrogen gas recharged into this storage cubic. With this change, its specific weight hydrogen storage capacity could be estimated from Equation (2):

\[
W_t = \frac{n_h w_h}{n_s w_s + n_h w_h} = \frac{16 (1)}{10 (28) + 16 (1)} = 5.41 \%
\]  

(2)

The cubic model is the smallest solid-state repeating unit under the assumption of a crystalline microstructure. From this model, it is easy to construct other forms of basic building blocks for hydrogen storage. The nanoporous silicon structure could be imagined as assemblies of these basic building blocks. The first extended model is the column model; it has two subtypes as shown in Figure 5 with or without corner silicon atoms. For the column model with corner silicon atoms, it has a model structure as shown in Figure 5(a). Since some surface is merged, the effective storage surfaces have changed; its storage capacity will be reduced accordingly. Its weight hydrogen storage capacity could be estimated from Equation (3):
W_t = \frac{H_a}{SH_a} = \frac{(20 \ N + 4)}{28(13 \ \frac{N}{N+1} + (20 \ \frac{N}{N+4})}

(3)

Where N = the number of basic cubic units

\[ H_i = n_hw_h \]

\[ SH_i = n_s w_s + n_h w_h \]

For i = a, b, c, d

As shown in Figure 6, its limit value can be calculated by the following equation

\[ \lim_{N \to \infty} W_i = \lim_{N \to \infty} \frac{\left( 20 + \frac{4}{N} \right)}{28\left( \frac{13}{N} + \frac{1}{N} \right) + \left( 20 + \frac{4}{N} \right)} = \frac{20}{28(13) + 20} = 5.21\% \]

(3a)

Similarly, for the column model without silicon at the corner as shown in Figure 5(b), its capacity will be further reduced. Its weight hydrogen storage capacity could be estimated from Equation (4):

\[ W_i = \frac{H_b}{SH_b} = \frac{(12 \ N + 4)}{28(9 \ N + 1) + (12 \ N + 4)} \]

(4)

When N increases to a large number, its storage capacity will approach to its limit value. As shown in Figure 6, its limit value can be calculated by the following equation

\[ \lim_{N \to \infty} W_i = \lim_{N \to \infty} \frac{\left( 12 + \frac{4}{N} \right)}{28\left( \frac{9}{N} + \frac{1}{N} \right) + \left( 12 + \frac{4}{N} \right)} = \frac{12}{28(9) + 12} = 4.54\% \]

(4a)

Another basic structure is a plate model. It also has two subtypes. Figure 7 illustrates their nanostructures. Similar to the column model, one plate model type is with silicon at the corner as shown in Figure 7(a), and the other one without silicon atoms at the corner as shown in Figure 7(b). Their weight hydrogen storage capacity can be estimated from Equations (5) and (6), respectively:
\[ W_t = \frac{H_c}{S H_c} = \frac{(8 N^2 + 24 N - 8)}{28(10 N^2 + 6 N - 2) + (8 N^2 + 24 N - 8)} \]  \hspace{1cm} (5) \\
\[ W_t = \frac{H_d}{S H_d} = \frac{(8 N^2 + 8 N)}{28(10 N^2 + 2 N + 2) + (8 N^2 + 8 N)} \]  \hspace{1cm} (6)

Where, \( N \) is the number of basic cubic units in one direction.

As shown in Figure 8, when \( N \) increases to a big number, their storage capacities become

\[
\lim_{N \to \infty} W_t = \frac{\lim_{N \to \infty} \left( 8 + \frac{24}{N} - \frac{8}{N^2} \right)}{28 \left( 10 + \frac{6}{N} - \frac{2}{N^2} \right) + \left( 8 + \frac{24}{N} - \frac{8}{N^2} \right)} = \frac{8}{28(10) + 8} = 2.78\% \]  \hspace{1cm} (5a)

\[
\lim_{N \to \infty} W_t = \frac{\lim_{N \to \infty} \left( 8 + \frac{8}{N} \right)}{28 \left( 10 + \frac{2}{N} + \frac{2}{N^2} \right) + \left( 8 + \frac{8}{N} \right)} = \frac{8}{28(10) + 8} = 2.78\% \]  \hspace{1cm} (6a)

Figure 7. Silicon plate model with \( N = 2 \).

Figure 8. Storage capacity ratio vs. plate size. variable

**Conclusions**

Based on the face center diamonds cubic model, Cubic, Column, Plate type hydrogen silicon storage models are developed. In each case, two different corner types are considered. The conclusions can be summarized as follows:

1. Cubic type crystalline structure has the highest hydrogen storage potential; its weight storage capacity limit is 5.77%.
2. Column type silicon crystalline structure has the second best hydrogen storage potential, its weight storage capacity limit is 5.21% when the column gets longer.
3. Plate type crystal structure has the worst hydrogen storage potential; its weight storage capacity limit is 2.78% when its dimension becomes larger.
References


