

## บทความวิชาการ

# การกำเนิดของ Organic Semiconductors Organic Semiconductors Meet the World

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## Introduction

Today, semiconductor technologies are focused on making electronic devices smaller with more sensitive in a specific application in mind. The semiconductor substrate is one of the most important parts of a molecular sensitive device. Basically, semiconductors are used to sense and transfer or carry signals. What is needed to improve the ability of devices is making the semiconductor more sensitive to the specific target. One way to accomplish this is to modify the surface of the semiconductor. By taking advantage of organic and inorganic material properties, semiconductor technologies have advanced significantly. By applying different organic molecules at the semiconductor surface the properties of the semiconductor could be changed.

## Characteristic of group IV reconstructed semiconductor surfaces

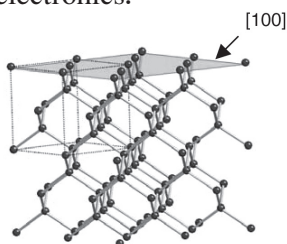
Group IV materials, including silicon (Si), and germanium (Ge), is one of the most interesting classes of semiconductors for a number of developing technologies. Si and Ge have the diamond lattice structure as shown in Figure 1. Every atom has a covalent bond with four neighbor atoms and has tetrahedral coordination. Once the crystals are cut in a plane perpendicular to the [100] lattice direction, the atoms at the interface are only bound to two other atoms, leaving two unpaired electrons for surface atom; which are known as “dangling bonds”. The crystal structure stabilizes by forming a reconstructed structure. (100) Crystal faces of Si and Ge all exhibit similar surface reconstructions in which pairs of surface atoms move together, bond, and form dimers.

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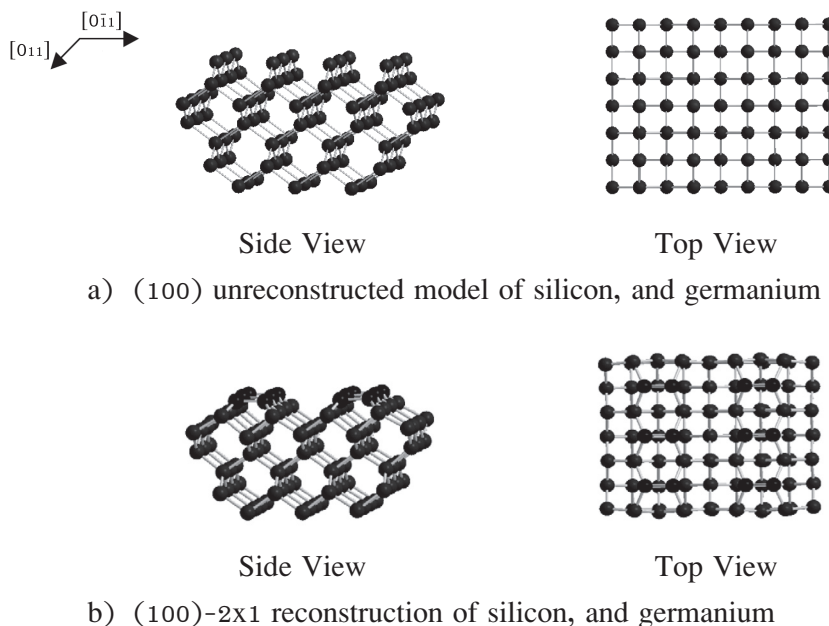
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The reconstructed structure contains dimer rows along the  $[011]$  direction. The  $(100)$  unreconstructed and reconstructed models of Group IV elements (silicon, and germanium) are shown in Figure 2. The bonding between the atoms or dimer bonds can be described in terms of a strong  $\sigma$ -bond and a weak  $\pi$ -bond. The  $\pi$  bond strength of Si  $(100)$  and Ge  $(100)$  is  $\sim 0.1$ - $0.2$  eV (10-20 kJ/mol). The  $\pi$ -bond character of surface dimers is much weaker than that of analog alkene molecules ( $\sim 2.6$  eV or 260 kJ/mol) and the surface dimers are more reactive of the increased reactivity is due to the lattice strain and reduced orbital overlap within the  $\pi$ -bond. Si  $(100)$  and Ge  $(100)$  surfaces become the most studied Group IV semiconductor surfaces because there are so many applications in molecular electronics.



**Figure 1** The crystal unit cell of silicon and germanium. The surface crystal structure exposed to a unit cell.



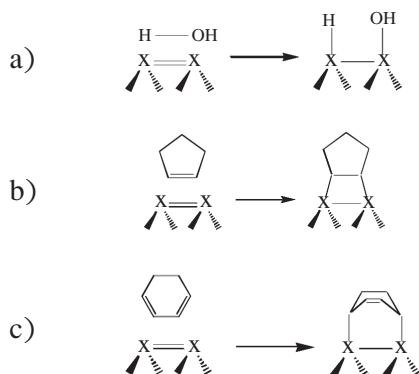
**Figure 2** Models of Group IV; Si, and Ge, semiconductor crystal a)  $(100)$  unreconstructed structure b)  $(100)$ - $2 \times 1$  reconstructed structure: rows of dimers are formed by a  $\sigma$ -bond and  $\pi$ -like interaction in the  $[1\bar{1}1]$  direction and dimer rows along  $[011]$  plane. Illustrations are provided by Prof. C. Michael Greenlief.

The  $\pi$ -bonds of Si and Ge dimers are distorted due to the nonplanar nature of the bonds and the underlying bulk substrates. Early studies showed that the dimers of the Si (100) and Ge (100) surfaces are tilted because of charge transfer from the “down” atom to the “up” atom. The general lattice characteristics of Si and Ge are identical with only the lattice spacing being different. The germanium lattice constant is 5.66 Å, which is slightly larger than that of silicon (5.43 Å).

### The reactivity of Si (100)-2x1 and Ge (100)-2x1 surfaces with organic molecules

#### a) Addition reaction

The double bond-like character of the dimer has been studied previously. It is known that the Si (100) and Ge (100) semiconductor surfaces provide the reactive sites for organic reactions. Small molecules such as H<sub>2</sub>O and H<sub>2</sub>S can react with dimers on the surface via an addition reaction [1]. The attachment of organic molecules to the (100) surfaces of crystalline silicon [2] and germanium [3] by cycloaddition reactions is also receiving attention. Many studies showed the possibility of a cycloaddition reaction on semiconductor surfaces. The dimers can react with unsaturated hydrocarbons such as cyclopentene and 1,5-cyclooctadiene, via a [2+2] cycloaddition reaction to form a four-member ring at the interface [2]. Moreover Si and Ge surface dimers can act as dienophile. Conjugated unsaturated hydrocarbons such as 1,3-cyclohexadiene can add across the dimers via [4+2] cycloaddition reaction or Diels-Alder reaction [4]. From many studies of the interaction of organic alkenes with Si and Ge surfaces, it is clear that there is the transfer of electrons from the C=C double bond to the surface.



**Figure 3** a) Addition reaction of H<sub>2</sub>O with surface dimer<sup>(2)</sup> and b) [2+2] cycloaddition reaction of cyclopentene with surface dimer<sup>(3)</sup> and c) [4+2] cycloaddition reaction of 1,3-cyclohexadiene with surface dimer<sup>(6)</sup> where x represents a surface dimer atom.

### b) Electrophilic and nucleophilic reactions

Not only do the surface dimers have a  $\pi$ -bond character but another interesting feature is that surface dimers can exhibit both electrophilic and nucleophilic character. Tilting of the dimers results in charge transfer between the down and up atoms within the dimer pair. The overall effect is that the down atoms have a slight positive charge relative to the up atoms of the dimer. Thus, the down dimer atoms, are the electron-deficient, and can act as an electrophile. While the up dimer atoms, which are the electron-rich, can act as a nucleophile.

Recently several research groups have been exploring the electrophilic and nucleophilic behavior of semiconductor dimers. Robert J. Hamers, a professor of chemistry at the University of Wisconsin, Madison and his research group modeled the nucleophilic behavior of surface dimers in the dissociate adsorption of amines. Some of their studies investigated the interaction of aliphatic and aromatic amines on semiconductor surfaces. The team discovered that the N lone-pair electrons in the amines were good sources for electron donation and the molecules react with the electrophilic site in the dimers [5, 6].

In order to study the reactions of organic molecules with surfaces, there are many surface analysis techniques available depending on what one would like to know about a surface. There is a wide variety of surface measurements can be used to monitor the change at the interface such as STM, HREELS, LEED or TDS. One of the most powerful classes for surface analysis techniques is Electron spectroscopy. Electron spectroscopy surface analytical techniques (AES, XPS, and UPS) can be used to investigate the surface interactions both qualitatively and quantitatively. Details of these techniques are briefly shown in Table 1.

**Table 1** Some types of surface analytical techniques

Analytical technique	Energy source	Signal detected	Detection limit	Depth resolution	Probe size	Applications
Auger Electron Spectroscopy (AES)	Electrons with energy of 5-30 keV	Auger electrons (100-2500 eV) from near surface atoms	0.1-1 at %	< 2 nm	100 nm	Surface composition

**Table 1 (continued)**

Analytical technique	Energy source	Signal detected	Detection limit	Depth resolution	Probe size	Applications
X-ray Photoelectron Spectroscopy (XPS)	X-ray Photon with energy of 200-2000 eV	Photoelectron from near surface atoms	0.01-1 at %	1-10 nm	10 $\mu\text{m}$ - 2 mm	Core level Surface analysis of organic and inorganic materials
Ultraviolet Photoelectron Spectroscopy (UPS)	UV Photon with energy of 10-45 eV	Photoelectron from near surface atoms	-	< 2 nm	10 $\mu\text{m}$ - 2 mm	Valence level surface analysis of organic and inorganic materials

The growing importance of organic films in semiconductor technologies has led to increased research. By using the combination of surface sensitive techniques, it is believed that the chemistry at the interface of the semiconductor can be determined.

In order to make organic semiconductors for electronic applications, it is important to have the reactive sites at the interface available for the target molecules to react or bind with. Moreover, controlling the order of the organic molecules to get a highly ordered adlayer at the interface is important for these potential applications in a wide variety of areas, such as molecular electronics, sensors and biotechnology. The important of depositing organic molecules on semiconductor surface becomes extensively researched for a past decade. It is believed that in the next few decade we could have a small device which the properties controlled by a few layer thick of the functionality of organic molecules at the interface.

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