



## Review

## Functionalization of flat Si surfaces with inorganic compounds—Towards molecular CMOS hybrid devices

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## ABSTRACT

Covalent modification of flat silicon surfaces is a key step in integrating CMOS technology and molecular electronics that may lead to novel hybrid microelectronic devices. While much of the research has been focused on the functionalization of Si by organic compounds, interest in the functionalization with metal-containing species has intensified in recent years because of the unique attributes of inorganic species including rich redox characteristics and high ground state spins. Described in this short review are (i) synthetic approaches to immobilize inorganic compounds; (ii) structural, spectroscopic and voltammetric techniques for characterization of molecular layers; and (iii) preliminary device fabrication.

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**Abbreviations:** ALD, atomic layer deposition; CEG, cathodic electrografting; CVD, chemical vapor deposition; CV, cyclic voltammetry;  $I_D$ , drain current; IPES, inverse photoemission spectroscopy;  $k_0$ , rate of electron transfer; MOSFET, metal–oxide–semiconductor field effect transistor; NHE, normal hydrogen electrode; OCP, open circuit potential; SAM, self assembled monolayer; STM, scanning tunneling microscopy; UHV, ultra high vacuum; UPS, ultraviolet photoelectron spectroscopy;  $\nu$ , scan rate ( $V s^{-1}$ );  $V_T$ , threshold voltage; WCA, water contact angle; XPS, X-ray photoelectron spectroscopy.

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## 1. Introduction

The continuous geometrical scaling of Si-based CMOS (complementary metal–oxide–semiconductor) transistors faces a multitude of technical hurdles that challenges materials sciences and engineering, such as the lack of effective dielectric materials at nanometer scale and an ever increasing power density. Hybrid transistors that incorporate organic/inorganic molecules into embedded interfaces of CMOS devices have been speculated as a promising alternative [1].

An essential starting point for such hybrid devices is the covalent attachment of molecules to a flat Si surface, which was first demonstrated by the formation of alkyl monolayer over both hydrogen passivated (H–Si) Si(100) and Si(111) surfaces [2]. Since then, organic functionalization of flat Si surfaces has received intense interest from both materials scientists and engineers, and the efforts have been reviewed many times [3–9]. In comparison with the development of organic functionalization, progress in inorganic modification of flat Si surfaces is lagging. It is noteworthy that coordination and organometallic compounds often possess physical attributes that are desirable for electronic devices, including the ability to store one or more electrons per molecule, to exhibit high spin and function as a single molecule magnet. These useful physical attributes are more difficult to realize in organic species without compromising molecular stability. It is noted that the metal–(coordination compounds)–metal junctions have displayed interesting device characteristics such as the Coulomb blockade, Kondo effect and negative differential resistances [10–13], demonstrating the advantage of both charge flexibility and molecular magnetism of inorganic compounds as the active components. In this contribution, we wish to survey the nascent efforts in covalent modification of flat H–Si surfaces with inorganic species and the preliminary results of electrical and magnetic device studies.

## 2. Background

The requirement for hybrid devices arises from the need to (a) work within current device fabrication techniques; (b) use existing infrastructure; and (c) develop an understanding of the influence of organic and inorganic species on the local and bulk physical and electronic properties of silicon. The two relevant silicon surface orientations are Si(100) and Si(111). Though much research has been based on Si(100) due to its broad use in industry, Si(111) is more common in a laboratory setting due to the ease of obtaining an atomically flat hydrogen passivated surface via simple chemical etchings [14–16], which facilitates further modification by “wet” chemistry methods. As Si(100) is the primary surface used in the micro-electronics industry much of the recent work has focused on this surface, despite the requirement of more stringent preparation procedure. Nevertheless, the surface has been shown to play a minimal role in electron transfer rates and stability characteristics of bound molecules allowing studies using Si(111) in laboratory settings to be relevant [17]. The most common functionalization is through the formation of a Si–C bond due to the high strength (Si–C,  $\approx 370$  kJ) of the bond, while the formation of Si–O bond (Si–O,  $\approx 368$  kJ) has been investigated as well. The formation of the Si–C bond results in a more stable system and higher electron transfer rates owing to the less polar nature of Si–C vs. Si–O [4,18]. Molecular passivation of the Si surface can be achieved using two distinct methods: (a) UHV conditions; (b) ambient conditions (wet chemistry technique). The former method has the advantage of being ultra clean and readily integrated with STM and XPS to yield structural details of the passivated surfaces in high precision, but is obviously demanding on infrastructure. The wet technique, on the other hand, requires nothing beyond the setup typical of organic/inorganic synthesis that is accessible to most chemists and biologists. This review will be limited to the passivation performed using wet techniques.

### 2.1. Bulk silicon

Silicon is an intrinsic semiconductor with an indirect band gap of 1.12 eV and an intrinsic conductivity of  $4.3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . To increase the conductivity, group IIIA elements (B, Al, Ga) or group VA elements (P, As, Sb) are used as dopants resulting in *p*- or *n*-type,

**Table 1**  
Physical properties of the Si surface [16,19].

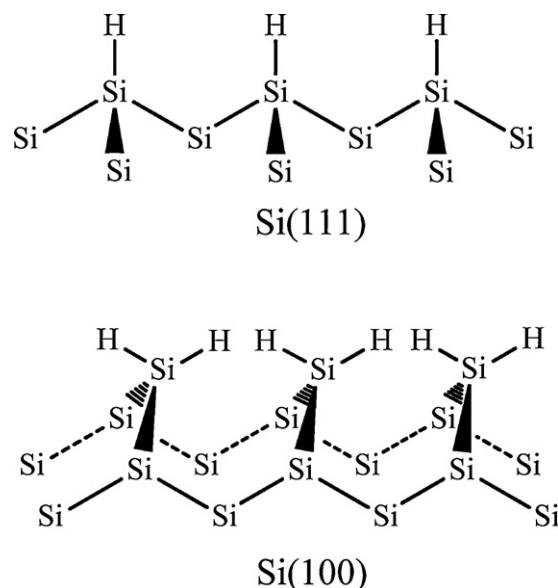
	Si(100)	Si(111)
Density (atoms $\text{cm}^{-2}$ )	$6.78 \times 10^{14}$	$15.66 \times 10^{14}$
Atomic spacing (Å)	5.43	3.13
Surface energy ( $\text{J cm}^{-2}$ )	2.13	1.23

respectively. The relevant data for Si(100) and Si(111) are listed in Table 1.

### 2.2. Surface preparation

Passivation is arguably the most important step for the functionalization of silicon. The surface is most often passivated by hydrogen, though halogens have also been used. Passivation is achieved by etching silicon oxide using HF for Si(100) and HF or  $\text{NH}_4\text{F}$  for Si(111), respectively. Using these wet chemical techniques, the surface is rough at the atomic scale containing a mixture of SiH, SiH<sub>2</sub> and SiH<sub>3</sub>, which arise from terraces, steps, kinks or vacancies. The surface roughness can be characterized by the hydride formation on the surface with the ideal surfaces of Si(100) forming SiH<sub>2</sub> and Si(111) resulting in SiH (Scheme 1). Using either HF or  $\text{NH}_4\text{F}$  to passivate Si(111) will result in the presence of both SiH and SiH<sub>3</sub>, while a mixture of  $\text{NH}_4\text{F}$  and HF results in mostly SiH [4,19].

Prior to passivation, a Si wafer needs to be free of microcontamination, namely ions, metals, hydrocarbons, and particles. The most commonly used cleaning methods are modifications of the RCA process developed in 1970 by Kern and Poutoinen [20]. Photoresist and large particles are removed by solvents (namely acetone, toluene and methanol), and the wafer is then washed in a heated mixture of sulfuric acid and hydrogen peroxide followed by rinsing with ultra-pure water ( $18 \Omega$ , UP4W) to remove organic contaminants. The initial layer of silicon oxide is then etched by dipping the wafer into an HF solution and rinsing with UPW. The wafer is subsequently placed into a mixture of ammonia hydroxide and hydrogen peroxide, followed by rinsing with UPW to remove many metal contaminants. The etching to obtain a flat Si(111) surface is then accomplished using either a 1–4% HF solution for 1–2 min, a 40%  $\text{NH}_4\text{F}$  solution for 10–15 min, or a mixture of both solutions. Although  $\text{NH}_4\text{F}$  etching is more time consuming, it is much less haz-



**Scheme 1.** Idealized hydrogen terminated surfaces.

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