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March 7, 1995

Dr. George Wright
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Dear George,

Enclosed please find three copies of a final report for my ONR grant titled: *Structural and Electronic Properties of Adsorbates on Semiconductors, Metal-Semiconductor Interfaces and Semiconductor Heterojunctions*, ONR Grant No. N00014-89-J-1290.

Sincerely,

Arthur J. Freeman
Morrison Professor of Physics

jb
Encl.

cc: J. Chiappe, ONR, Chicago
Defense Tech. Info. Center ✓
Director, Naval Res. Lab.
G. Goldberger, ORSP, NU

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13. ABSTRACT (Maximum 200 words)

Studies of the electronic structure of adsorbates on metal-semiconductor and semiconductor-semiconductor interfaces and semiconductor surfaces were carried out using the molecular cluster LCAO-DVM method (as developed into the DMol program) also in a full potential local (spin) density approach. The new capability of DMol to calculate atomic forces allows automatic geometry optimization and allowed us to study atomic relaxation and reconstruction at the surfaces and interfaces with and without adsorbates. The method calculateed variationally self-consistent highly precise solutions of the local density equations with which to determine the structural and electronic properties of the system. Specific problems addressed included studies of: (i) semiconductor heterojunctions (and their bulk constituents) such as Sn/Ge, and (ii) adsorbates on silicon and germanium. The research led to the development of general concepts and simpler theoretical models with which to understand the electronic structure and the relevant parameters governing the interaction between the adsorbate and the substrate. Predictions of theory were compared with experiment. Accurate total energy investigations were undertaken to determine from first principles, equilibrium, internuclear distances, vibrational frequencies, separations and positional (geometric) bonding configurations.

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FINAL REPORT FOR

ONR Grant No. N00014-89-J-1290

STRUCTURAL AND ELECTRONIC PROPERTIES OF ADSORBATES ON SEMICONDUCTORS, METAL-SEMICONDUCTOR INTERFACES AND SEMICONDUCTOR HETEROJUNCTIONS

Period of Performance: November 1, 1991 to October 31, 1994

A.J. Freeman, Principal Investigator

I. Background Perspective

An enormous research effort has been concentrated on the metal/silicon interface. Much less work has been done on the metal/Ge interface. In this grant we have concentrated on both Si and Ge as substrate. We present results of extensive studies on both of these in what follows. This will give an indication of the power of the new methods developed and the type of information obtained from these studies.

The motivation for all this effort comes from both technological and fundamental scientific interest in the metal/silicon interface, which is especially important in the manufacture of electronic devices. The clean Si(100) surface shows a dominant 2x1 structure,[1] although some higher-order structures, such as c(4x2), p(2x2), c(2x2) and c(4x4), are also reported. The 2x1 reconstruction is generally believed to be due to the well-known Si dimer formation.[2] This surface is still chemically reactive since there is a dangling bond associated with each surface Si atom. Therefore, different atoms adsorbed on Si(100) will result in different structural and electronic property changes.

The chemical reactions of various metals with Si can be grouped as follows: (i) a very active chemical reaction which forms metal silicide at the interface such as Mo/Si and Ni/Si; (ii) passivation of the Si surface by forming a metal overlayer and removing the Si(100)2x1 reconstruction, e.g., As/Si and Sb/Si; (iii) medium interaction by adsorbing on specific sites of the Si surface and inducing more complex reconstruction; for example, In on Si can have (2x2) and (4x3) reconstructions depending on the temperature; (iv) less reactive so that the underlying Si substrate does not change upon metal adsorption, e.g., alkali metals on Si.

One of the most important characteristic features of the metal-Si interface is the nature of the potential barrier between the Fermi level in the metal and the majority carrier's band edge of the semiconductor - known as the Schottky barrier at that interface. This potential barrier is of central importance in determining the performance of Si devices. Since the chemisorption of metals on the Si surface is the early stage of the chemical reaction of metals with Si, their study is an important

first step to understand the mechanism of Schottky barrier formation, the bonding between metal and Si and the metal induced change of surface states.

II. Results

Our study on the metal/silicon interface for the last year has been focussed on the alkali metal (Na) and group V metals (As and Sb) on Si(100) surface. The main results are summarized below. As an appendix, we include a preprint of a paper we are about to submit entitled "*Ge(100) 2x1 and c(4x2) Surface Reconstructions Studied by ab-initio Total Energy Molecular Force Calculations*". This will indicate the nature and results of our study of the Ge(100) surface reconstructions. As a next step, we will study alkali metals adsorbed onto the Ge(100) surface.

A. Na adsorption on Si(100)2x1

We have studied Na chemisorption on the Si(100) surface.[3,4] There are four possible adsorption sites on Si(100)(2x1), i.e. pedestal, cave, bridge and valley bridge sites and they are simulated by cluster models ranging from 22 to 77 atoms. A preliminary calculation excluded the bridge site because it has far lower adsorption energy than the other sites. For the remaining three sites, we calculated Na adsorption on both the unrelaxed silicon substrate and the relaxed substrate, since it is possible that surface relaxation might be of some relevance in the determination of the correct adsorption site. The calculated adsorption energy is shown in Table 1. When the substrate is unrelaxed, the cave site has the highest adsorption energy followed closely by the pedestal site with a difference of only 0.04~eV. It is hard to distinguish which is the most stable site with such a small energy difference. By taking into account the surface relaxation, one can see that the highest adsorption energy is now obtained for the cave site with a difference that is 0.17~eV higher than the pedestal site. On the other hand, the calculated bond lengths of Na-Si and Si-Si at cave site are the closest to the experimental results among the three sites. Thus, the cave site is the most favorable adsorption site for Na.

Table 1: Na adsorption energies (in eV) for the cave, pedestal and valley bridge sites in the cases of unrelaxed and relaxed Si(100)2x1 substrate.

	unrelaxed	relaxed
Cave	2.03	2.22
Pedestal	1.99	2.05
Valley-Bridge	1.72	1.92

As to the nature of the bonding between Na and Si, we found it is a mixture of ionic and covalent bonding. When compared with other groups of metal on Si(100), Na forms relatively weak bonding with Si. Because of this weak bonding, the Si(100)2x1 reconstruction remains unchanged when Na adsorbs on the surface.

B. Group V Metals on Si(100)

We first determined the optimal adsorption site of a single As or Sb atom on Si(100)1x1 and Si(100)2x1.[5,6] There are four possible adsorption sites for each surface, and they are simulated by 8 clusters having 22 to 26 atoms. For As and Sb on Si(100)2x1, the bridge site has the highest adsorption energy and therefore is the most stable site among the four possible sites studied. For As and Sb on Si(100)1x1, we have different results which show that As prefers to adsorb on the bridge site and Sb on the hollow site. One does not expect such a result because, experimentally, As and Sb shows similar behaviour on the Si(100) surface. This discrepancy is resolved when metal-metal interactions are included in the calculation. To do that, we chose another set of larger clusters and put two metal atoms on several sites and in two different orientations with respect to the Si dimer on the clean Si(100)2x1 surface. The calculated results show that the bridge site has the highest adsorption energy for both As and Sb. The final results of our structural model are shown in Table 2 together with the experimental values. There is a quite good agreement between our theoretical results and experiment.

In the meantime, we found that As and Sb adsorbed on the Si(100) surface induce large unbalanced forces in the substrate because of the strong covalent bonding between metal and Si. This lead us to study the metal-induced passivation of Si(100)2x1. The study was conducted on a $Sb_3Si_{27}H_{32}$ cluster which includes a combination of two bridge sites and one cave site. If we put two metal atoms on the bridge site and one atom on the cave, we found a strong force in the substrate that tends break the Si dimer. Indeed, breaking the Si dimer would gain an extra 0.52~eV/dimer. The result is that the Si(100)2x1 reconstruction is removed by the adsorption of As or Sb atoms.

Table 2: Optimized structural parameters for As and Sb dimers on Si(100)(1x1) calculated from a 63 atom cluster model: h is the vertical height of the metal atom from the Si surface, and $d_{As\text{-}Si}$ and $d_{Sb\text{-}Si}$ stand for the closest distances between the metal and Si atom; distances between two As or Sb atoms are represented by $d_{As\text{-}As}$ and $d_{Sb\text{-}Sb}$. All distances are in unit of Å.

		Present	Theo.[2]	Exp.
	h	1.43	1.41	1.26±0.01[b], 1.43[b]
As/Si	$d_{As\text{-}Si}$ 2.45	2.44	-	
	$d_{As\text{-}As}$ 2.52	2.55		2.55±0.01[c]
	h	1.73	-	1.74±0.05[d]
Sb/Si	$d_{Sb\text{-}Si}$ 2.61		-	2.63±0.04[d]
	$d_{Sb\text{-}Sb}$ 2.93		-	2.88±0.03[d]

a Ref.[7]

b Ref.[8]

c Ref.[9]

d Ref.[10]

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A.J. FREEMAN
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a. PAPERS SUBMITTED TO REFEREED JOURNALS (AND NOT YET PUBLISHED)

None

b. PAPERS PUBLISHED IN REFEREED JOURNALS (14)

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c. BOOKS (AND SECTIONS THEREOF) SUBMITTED FOR PUBLICATION (2)

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d. BOOKS (AND SECTIONS THEREOF) PUBLISHED (4)

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i. CONTRIBUTED PRESENTATIONS AT TOPICAL OR SCENTIFIC/TECHNICAL SOCIETY CONFERENCES (7)

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