

The Interaction of Atoms with GaAs[110] Surface using Local Softness Model

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Using the local version of the Hard and Soft Acids and Bases (HSAB) principle we have studied the reactive regions of the GaAs[110] surface upon chemical attack of atoms. Based on properties of the isolated reactants, the HSAB principle allow us to predict the most reactive sites of a polyatomic system. The surface was simulated by a cluster of 44 atoms and the calculations are performed at the ab initio Hartree-Fock level to determine its electronic properties.

I. Introduction and Procedures

The first-principles calculations of the interaction of a given surface with different atoms is known to require an immense computational effort. Hence, alternative approaches that can treat this problem in a more intuitive way would be very attractive.

In recent years it has been verified that, by the application of the *hard and soft acids and bases principle* (HSAB) in its local version, one can preview the most reactive sites of a surface (or molecule) in interactions. The local version of the HSAB principle can be stated as: *Given a system with different reactive sites, its hard regions prefer to interact with hard species whereas its soft regions prefer soft attacking groups to react.* Within the framework of the Density Functional Theory the local hardness, $\eta(\mathbf{r})$, and the local softness, $s(\mathbf{r})$, were defined by Parr and co-workers^[1]. By means of the method of finite differences one can define the local softness within the Hartree-Fock-Roothann scheme as the

difference of the local density of charge between different charge states of the system under consideration^[2]. This system depending on its electronegativity (the acid or base character), can give or receive electrons in a reaction with an atom. Hence, depending on the particular reaction we define,

$$\begin{aligned} s^+(\mathbf{r}) &= \rho^0(\mathbf{r}) - \rho^+(\mathbf{r}), \\ s^-(\mathbf{r}) &= \rho^-(\mathbf{r}) - \rho^0(\mathbf{r}), \\ s^0(\mathbf{r}) &= \frac{s^+(\mathbf{r}) + s^-(\mathbf{r})}{2}, \end{aligned}$$

for the local softness. The $s^+(\mathbf{r})s^-(\mathbf{r})$ is the local softness when the system (a surface in our case) have a value of electronegativity lower (greater) than that of the atom with which it interacts, because in this case it will donate (accept) electrons.

The Mulliken electronegativity of a given system is defined as

$$\chi = \frac{(IP + EA)}{2},$$

Table 1: Electronegativities and hardness values

	GaAs[110]	Cs	Na	Si	Ge	Sb	Br	Cl
χ (eV)	1.36	1.51	2.30	4.05	4.20	4.25	6.66	6.86
η (eV)	0.28	1.85	2.57	3.75	3.31	4.45	4.18	5.57

where IP and EA are the ionization potential and electron affinity respectively.

The global hardness can also be defined in terms of IP and EA as

$$\eta = \frac{(IP - EA)}{2}.$$

With these quantities, one can make the following analysis: (a) Compare the electronegativity of the atom to the surface work function. (b) Calculate the local softness s^+ , s^0 and s^- in appropriate planes for later analysis. (c) Determine the global hardness of the atom and of the surface. (d) Apply the local interpretation of the HSAB principle to select the most reactive site or sites.

We have studied the interaction of the GaAs[110] surface with several (Na, Cs, Si, Ge, Sb, Br, Cl) atoms. The geometry of the relaxed surface was obtained from experimental data^[3] and is shown in Fig. 1.

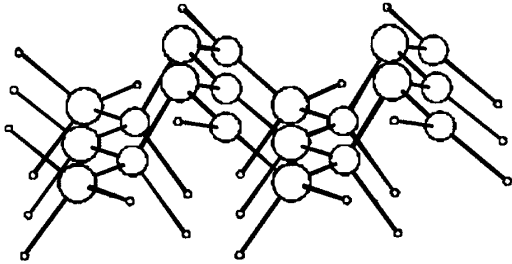


Figure 1. The cluster that simulates the GaAs[110] surface. The large, medium and small circles represent the As, Ga and H atoms, respectively.

The cluster that simulates the surface has 10Ga, 10As and 24H atoms. We have calculated the charge densities in the three states (+,0,-) for this surface using an effective-core-potential basis set^[4]. For the atoms we have used the Huzinaga's MIDI basis set plus one diffuse function^[5] to calculate the charge densities.

II. Results and discussion

In Table 1, we show the results for the electronegativities and global hardness. According to these values

one can see that the surface is less electronegative than all atoms, except Cs for which it is nearly equivalent. Thus, the interaction of these atoms with the GaAs[110] surface will occur with the surface acting like a base and we must look at the $s^+(\mathbf{r})$ countour maps. Also, since the atoms are harder than the surface, one must look at the regions of minimum values of softness. These are the regions of negative softness of $s^+(\mathbf{r})$, $s^+(\mathbf{r}) < 0$, and are given here for a selected set of planes, as shown in Fig. 2.

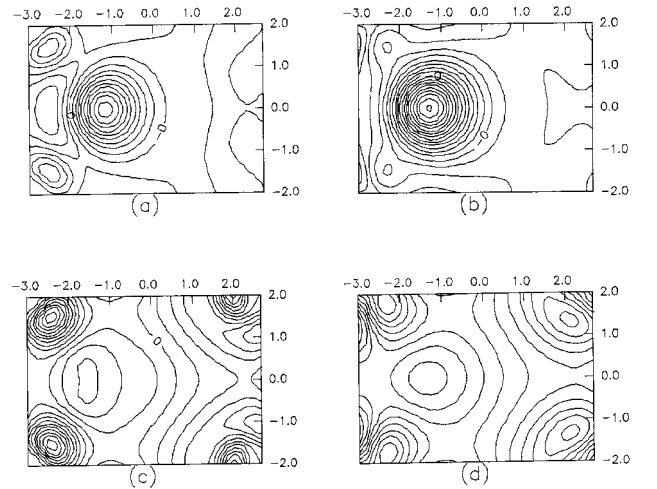


Figure 2. The a and b (c and d) maps give the $s^+(\mathbf{r})$ ($s^0(\mathbf{r})$) calculated at planes parallel to the GaAs[110] surface at 0.0 Å and 0.5 Å above the As surface atoms, respectively. The As atoms are at the corners of the planes and the Ga atom has coordinates (-1.772, 0.00).

For all atoms considered (except Cs) one can see that the region above the Ga atom and the region between Ga and As atoms are the most probable regions for the occurrence of interaction. These predictions are in agreement with several experimental results^[6] and the theoretical calculations^[7].

For the Cs atom, however, we must also consider the region determined by the $s^0(\mathbf{r})$ planes. Looking at the $s^0(\mathbf{r})$ countours one can see that the region behind the As atoms is also a probable one (see Figs. 2(c) and

(d)). Again, this prediction is in agreement with an experimental Scanning Tunelling Microscopy result^[8].

III. Summary

We have seen that with a simple calculation of charge densities of isolated reactants we can predict the most probable regions of interactions of a surface with different atoms with good experimental agreement.

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