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Observation of metal atoms adsorbed on H-terminated Si(001) surfaces by STM/STS and its consideration based on ab-initio molecular orbital calculations

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The authors try to establish a procedure of micro elementary analysis using STM/STS, which makes it possible to identify single metal atom on the H-terminated Si wafer surface. The elementary analysis is carried out by comparing the measured LDOS from STM/STS with the calculated one based on the first principle of quantum mechanics. To explain the measured LDOS, we calculated the wave function of a metal atom on the H-terminated Si(001) surface by ab-initio molecular orbital method. It is important to consider not only LDOS,but also the spatial distribution of the wave function from the Si surface.

1.INTRODUCTION

For the fabrication of ULSI devices in the next generation, it is indispensable to prepare cleaner Si surfaces than those used today.To meet this demand, an elementary analysis of the contaminated atoms at the atomic level is required.

In this work, a STM/STS[1] system is developed for establishing a micro elementary analysis, by which one atom adsorbed on the surface can be identified. Our analysis procedure consists of three parts. 1)We measure I-V characteristics of the tunneling junction at the site where an adsorbed metal atom exists. 2)the LDOS at the site is obtained by calculating $dI/dV \diagup I/V$[2]. 3)The elementary analysis is carried out by comparing the measured LDOS from STM/STS with the calculated one based on the first principles of quantum mechanics.

In this paper, we reveal the result of I-V characteristics obtained on an H-terminated Si surface with adsorbed metal atoms. Simulated electronic structures using ab-initio molecular orbital method are also given.

2.SIMULATIONS OF SURFACE ELECTRONIC STRUCTURES

In our calculations, we adopt AMOSS (Ab-initio Molecular Orbital System for Supercomputers; NEC) the program of an unempirical molecular orbital method. We use effective core potential method(ECP[3]) in molecular orbital calculations. This is based on the idea where only valence electrons of an atom are concerned in a chemical binding, and we can ignore the effect of inner electrons for basis functions. Thus electrons we have to take account of are four($(3s)^2(3p)^2$), nineteen ($(3s)^2(3p)^6(3d)^{10}(4s)^1$) and three($(3s)^2(3p)^1$) in a Si,Cu and Al atom, respectively. Furthermore eigenvalue E_i and eigenvector C_i are obtained from molecular orbital method and LDOS is given by the relations of

$$\Psi_i = \sum_{s,v} C_{sv,i} \cdot \varphi_{sv} \qquad (1)$$

$$n_s(E) = \sum_{i,v} |C_{sv,i}|^2 \, \delta(E_i - E) \qquad (2)$$

where Ψ_i is a molecular orbital of i-th eigenvalue, $\phi_{s,\nu}$ is an atomic ν-orbital of s-atom, $n_s(E)$ is LDOS of s-atom, and $C_{s,\nu,i}$ is an atomic orbital coefficient of i-th eigenvalue. In Eq.(2) LDOS is expressed as streaks because it is a direct result of a molecular orbital calculation. Thus we give a Gaussian distribution to each streaky LDOS as follows:

$$n_s(E) = \sum_{i,\nu} |C_{sv,i}|^2 \exp\left\{-a(E_i - E)^2\right\} \quad (3)$$

where 'a' is a parameter that decides a width of a Gaussian distribution.

A cluster model containing 22 Si atoms is prepared. All the outermost Si atoms on the surfaces are terminated by H atoms. We bring a Cu atom or an Al atom close to the center of 4 Si atoms and fix it at the position where total energy of the system becomes minimum. The model is shown in Fig.1.

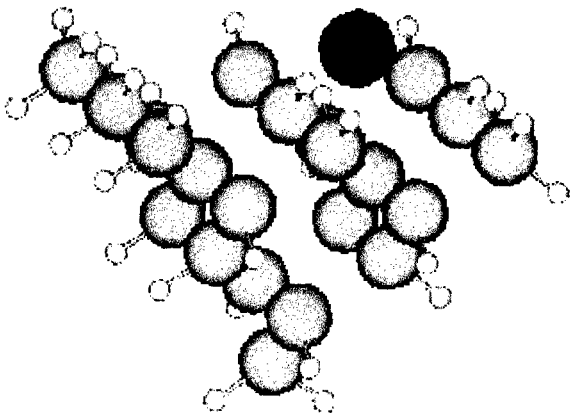


Fig. 1. Cluster model for simulations

On the configuration with the minimum total energy, we calculated LDOS of a Si atom on the surface.

Figure 2 is LDOS of a Si atom on the surface in the case ((a) the surface is terminated by H atoms, (b) a Cu atom is adsorbed on the surface and (c) an Al atom is adsorbed on the surface). Peaks in the bandgap indicated by A are seen only on the surface with a Cu atom or an Al atom, and cannot be seen on the H-terminated surface. Furthermore, the position and the height of the peak B are different from each other. Those facts show possibilities to identify a single metal atom on the Si surface.

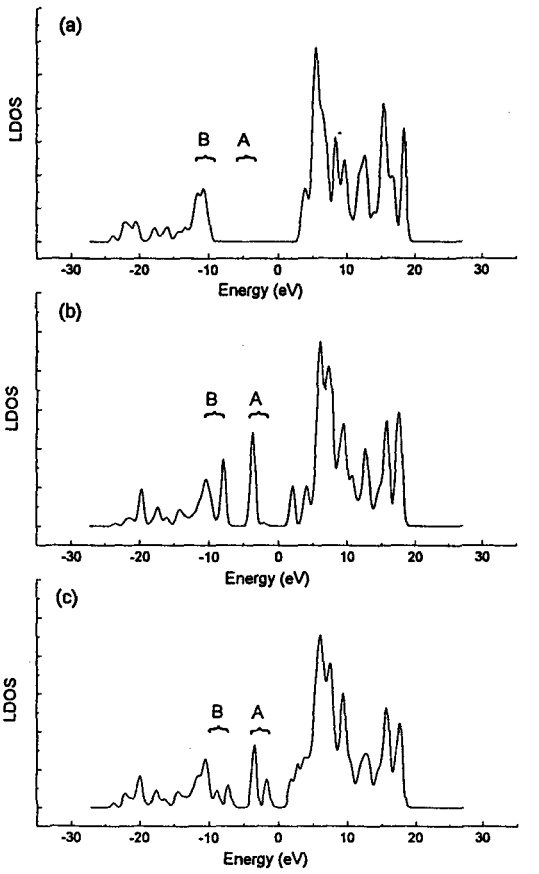


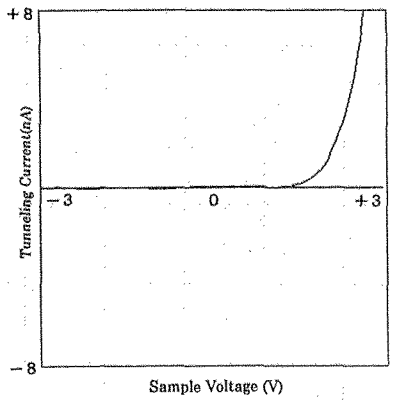
Fig. 2. LDOS of (a)H-terminated Si surface (b) the surface with Cu (c) the surface with Al

3.MESUREMENT OF I-V CHARACTERISTICS WITH STM/STS

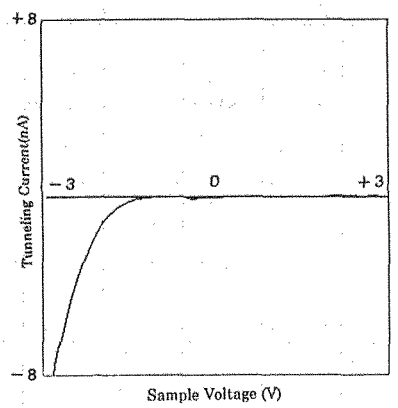
Based on the idea described in section 2, we performed STS mesurements and obtained LDOS on the Si surface with homemade STM/STS system. We have used p-type Si(001) wafer. The sample were dipped into HF solution to remove oxide layers and we prepared H-terminated surfaces. Figure 3 shows I-V characteristics on the H-terminated surface measured by STS. This

ult shows that no tunneling current is ected from the Si valence band to the STM

I-V characteristics were measured on the face polluted by Cu atoms(Fig.4). The face concentration of Cu atoms was 10^{14} oms/cm^2. No tunneling current is detected m the Si conduction band to the STM tip, ich is contrary to the result on the H-minated surfaces. Strikingly, these asured I-V characteristics (Fig. 3 and 4) completely different from the results ained by molecular orbital calculations(Fig. To explain the discrepancy, the spatial tribution of the wave function in both ence and conduction band should be sidered in the calculation.



. 3. I-V characteristic on the erminated Si



. 4. I-V characteristic on the erminated Si with Cu atoms

4.DISCUSSION OF EXPERIMENTAL RESULTS BASED ON A SPATIAL DISTRIBUTION OF WAVE FUNCTIONS

We calculated the spatial distribution wave functions for each energy level usir the model discussed in Section 2. We pa attention only to the central atom among nir atoms in the surface. Typical results a shown in Figs. 5 and 6.

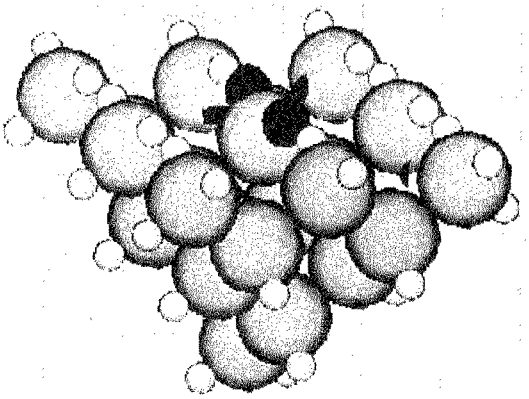


Fig. 5. Spatial distribution of the molecular orbital which forms valence band

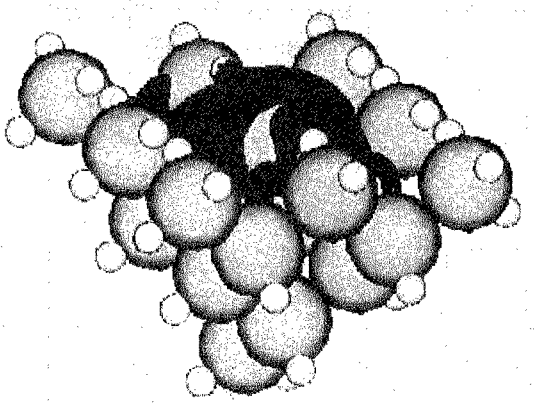


Fig. 6. Spatial distribution of the molecular orbital which forms conduction band

Figure. 5 shows a molecular orbital of the highest energy level in the valence band and Fig.6 is one of the lowest in the conduction band. The wave function forming the conduction band expands more spatially than that forming the valence band. This tendency is confirmed also in other wave functions.

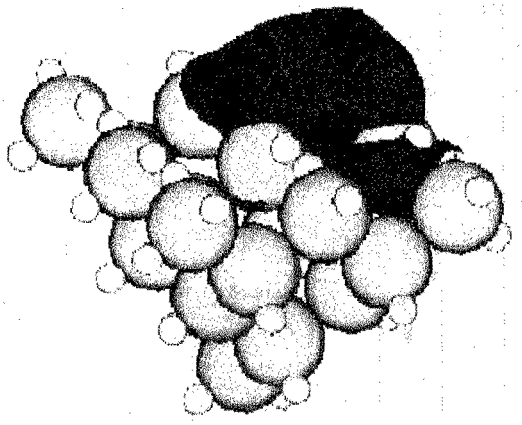


Fig 7. Spatial distribution of the molecular orbital which forms valence band

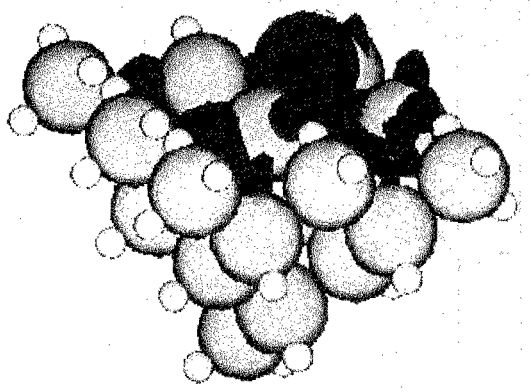


Fig 8. Spatial distribution of the molecular orbital which forms conduction band

Tunneling current appears only when the wave functions of a tip and a sample overlap with each other. In our experiment, after sample bias was set to positive, we fixed the tip at the position where the pre-determined tunneling current was detected.

Therefore, the tunneling current from conduction band was detected more easily than that from valence band because of the difference in the spatial distribution of molecular orbitals discussed above.

Next we performed the same calculation using the model of the H-terminated Si with a Cu atom. The spatial distributions of wave functions were given at the site of the Cu atom surrounded by 4 Si atoms.The result is shown in Fig. 7,8.

The result of this calculation is completely opposite to the one obtained by the model of the H-terminated Si. This is, however, consistent with the experimental result.

So we can conclude that I-V characteristics obtained by STM/STS are explained by considering the spatial distribution of wave functions. A larger model should be adopted ,however, to simulate the real surface. And this ab-initio molecular orbital method itself has some problems in its accuracy. So we should develop more accurate calculational method than that we adopted here.

5.CONCLUSION

In this work, we performed computational simulations by using ab-initio molecular orbital method. We showed that it was important to consider the spatial distribution of the wave function from the Si surface to explain I-V characteristics measured by STM/STS system.

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