The Absorption Mechanism of Hydrogen on the Aluminum Surface

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ABSTRACT

The ab initio molecular orbital calculations are carried out to elucidate the microscopic mechanism of the hydrogen absorption into aluminum caused by the mechanical removal of the surface in air. In the experiments, the importance of the existence of H_2O and that of defects introduced near the surface has been suggested. All calculations are performed by using the hydrogen-aluminum clusters based on the experimental results. It is found that there is a high potential barrier between the outside and the inside in the perfect clean surface model, while no conspicuous barrier appears in both the distorted cluster model with the dislocation and the model with oxygen near the hydrogen path. In the last model, it is suggested that the inner site is more stable than the outer site. These calculations support the experimental results.

1. Introduction

It is well known that the solubility of hydrogen in aluminum is very low; only 0.6 at.ppm in atmospheric hydrogen gas even just under the melting point.[1] The diffusive behavior of hydrogen in aluminum has been studied by surface-sensitive methods, such as thermal evolution and permeation methods.

Our thermal evolution experiments on aluminum annealed in hydrogen atmosphere have shown the following feature (see Figure 1); " **While the as-annealed sample evolves little hydrogen during heating, remarkable evolution occurs around 220 and 400°C after mechanical removal of the sample surface in air. In particular, the evolution rate peak at the lower temperature does not change by repetition of the surface removal and heating run.**" This suggests the possibility that hydrogen is introduced into aluminum by the mechanical removal of the surface in air. The source of hydrogen considered at first is water (H_2O) included in air.

In order to examine that the source of hydrogen is H_2O, the surface removal procedures were carried out in air, distilled water, acetone and ethanol. Figures 2 and 3 show the hydrogen evolution curves when the surface removal of a sample is repeated in air and in distilled water, respectively. The numbers in the figures indicate the average sample thickness after each surface removal. In both cases, a broad peak appears in the range 100-200°C, and the peak shifts to lower temperature as the samples becomes thinner. These imply that hydrogen does not merely adsorb on the surface but distributes inside the sample. In addition, the total evolution increases through the repetition of the surface removal in distilled water. On the other hand, as shown in Figure 4, no significant hydrogen evolution occurs when the surface is removed in acetone or in ethanol, which contain little water

The experimental results quoted above suggest that hydrogen is absorbed into aluminum by the reaction between the clean surface of aluminum and H_2O, and oxygen may play an important role on the absorption process. Here, it should be considered that many defects such as dislocations are necessarily introduced near the surface by the mechanical removal of the surface. By the way, the hydrogen absorption into metals by the reaction with H_2O has been only studied on metals with the high solubility of hydrogen, such as tantalum and palladium.

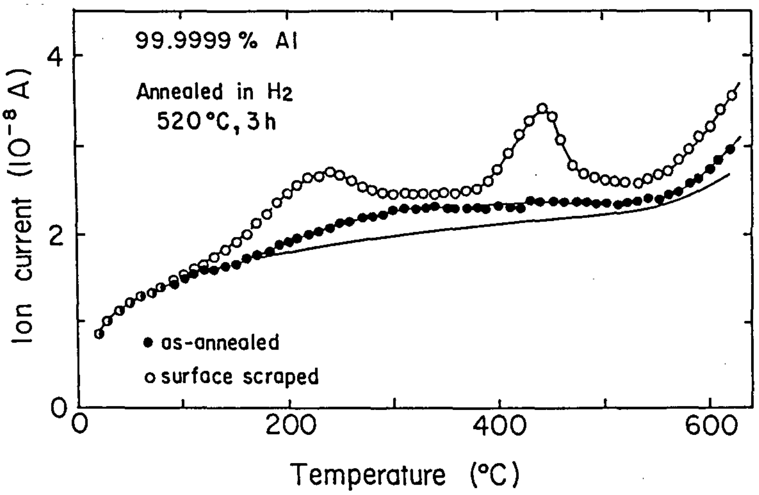


Figure 1

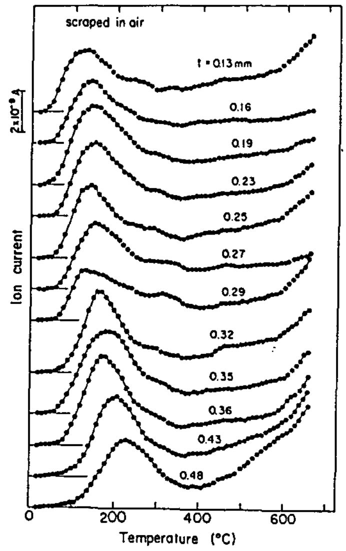


Figure 2

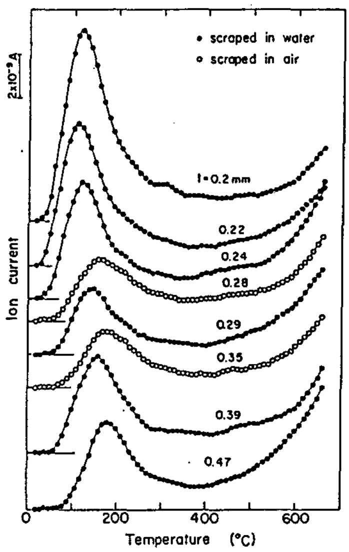


Figure 3

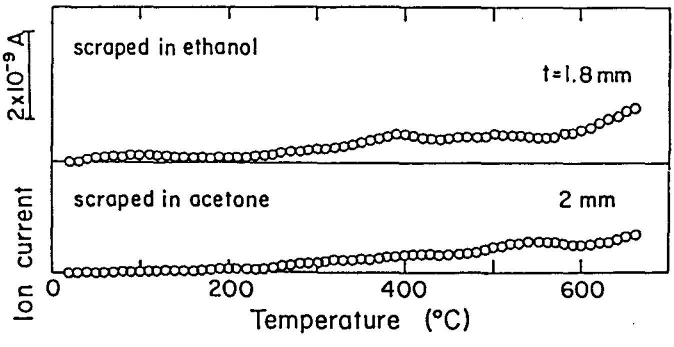


Figure 4

In this work, in order to study the microscopic mechanism on the surface in the hydrogen absorption process, the ab initio molecular orbital calculations were performed using hydrogen-aluminum cluster models. As the first step, they are carried out for the cleavage reaction of H_2O on the clean surface. Then the potential curves are shown for hydrogen absorption through the surface without lattice distortion. Furthermore, the effects of surface defects and oxygen are taken into account.

2. Method and models of calculations

2.1 Calculational method.

All calculations were carried out by means of ab initio molecular orbital method based on the general SCF LCAO formalism. The method essentially corresponds to Roothaan's Hartree-Fock equations for molecules, and considers all electrons and the interatomic interactions based on the first principle. The variational calculations lead to the usual secular determinant;
$|F(i,j)-E(j)S(i,j)|=0$, where $F(i,j)$ is the Fock matrix element between the i-th and j-th atomic orbital, $S(i,j)$ is the overlap integral between these orbitals, and $E(j)$ is the j-th molecular orbital energy. Ab initio calculations were performed by using the GAUSSIAN 86 program with a 3-21G basis set, which is the split valence contracted gauss type basis set, on the HITAC M680H and S820/80 computers in Institute for Molecular Science.

2.2 Models and assumptions.

As already described, hydrogen is introduced into aluminum when the surface is removed mechanically in the presence of H_2O. This phenomenon can be divided into the following two parts;

1) The adsorption of H_2O on the clean surface and the dissociation of hydrogen from H_2O.
2) The absorption of hydrogen into aluminum.

Furthermore, in the second part above, the following three cases are supposed;

2-1) The absorption from the perfect clean surface.
2-2) The absorption from the defective site.
2-3) The absorption when oxygen exists near the absorption site.

The calculations were carried out with model clusters which consist of a hydrogen and several aluminum atoms for simplicity. The linear Al_4/H_2O cluster (Model 1) as shown in Fig. 5 was used for case 1). For case 2-1), the (100) and (111) surfaces were selected and modeled by Al_5/H cluster (Model 2) for the former and by Al_4/H (Model 3) and Al_7/H ones (model 4) for the latter. They are shown in Fig. 6. For case 2-2), an edge dislocation through the surface was introduced as shown in Fig. 7, and the distorted Al_5/H cluster (Model 5) as shown in Fig. 8 was used. For case 2-3), the calculations were carried out on the (111) surface with $Al_4/OH/H$ (Model 6) and $Al_4/O/H$ (Model 7) clusters as shown in Figs. 9 and 10, respectively. In this case, OH and O were placed at the hollow site adjacent to the hydrogen path and fixed at the equilibrium points which were optimized using Al_3/OH and Al_3/O clusters, respectively. The distances between the surface and oxygen are 1.162525 Å and 0.542929 Å, respectively. Here, it should be noticed that case 2-3) corresponds to the early stage of surface oxidation.

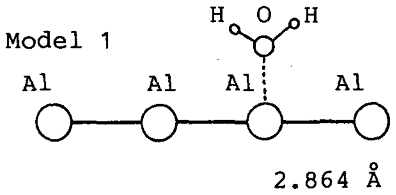


Figure 5: Linear Al_4/H_2O

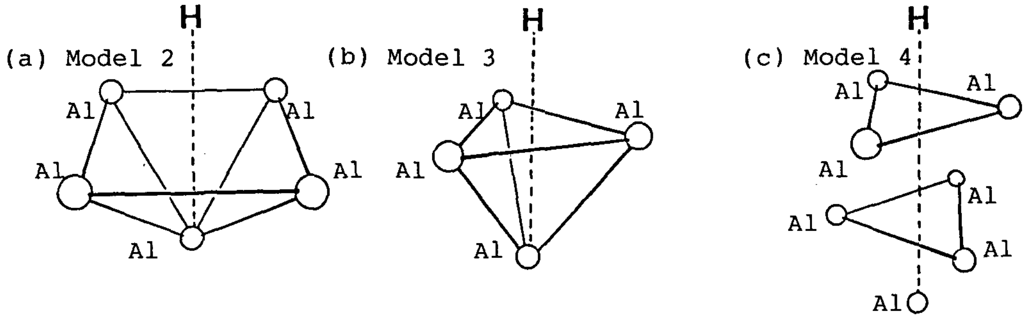


Figure 6: (a) Al_5/H (100) path, (b) Al_4/H (111) T_d path, (c) Al_7/H (111) O_h path.

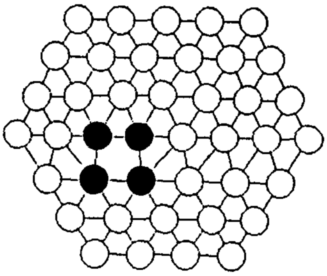


Figure 7: (111) surface with dislocation.

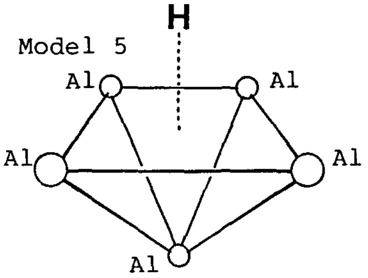


Figure 8: Distorted Al_5/H

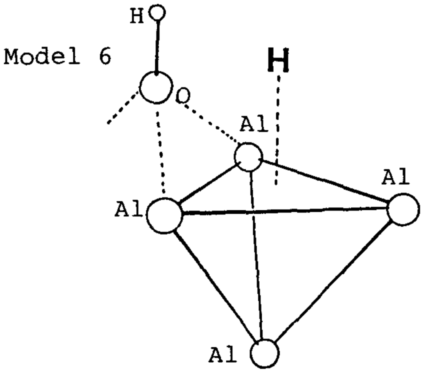


Figure 9 : $Al_4/OH/H$

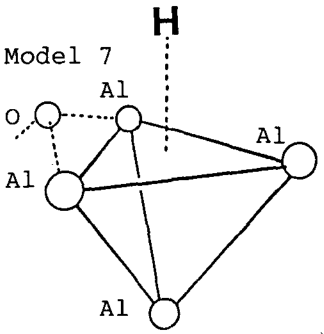


Figure 10: $Al_4/O/H$

In the present calculations, the lattice constant was fixed at 4.05 Å and the lattice relaxation with the approach of hydrogen was ignored. The potential curves were obtained along the absorption path perpendicular to the surface. Although vacancies have a notable effect on hydrogen absorption into aluminum [2-4], their effect was not considered in this work.

3. Results of calculations and Discussion

3.1 Adsorption and dissociation of H_2O

The calculation for the adsorption point of H_2O on the aluminum surface was carried out using Model 1. The geometry optimization shows that H_2O adsorbs on-top site with the Al-O distance of 2.06 Å and the binding energy of 0.83 eV. The same calculation performed by using H_2O and the Al_4 cluster as Model 3 shows no stable point at the hollow site.

The transition state for dissociation of hydrogen from H_2O was obtained using Model 1. The result is shown in Fig. 11. This reaction is the four center reaction, and Al_4 and H_2O are in the same plane. The activation energy obtained for the dissociation is 0.27 eV. The use of better basis set, as generally known, lower the activation energy, and on the real surface, more electrons should be supplied to H_2O. Thus the real activation energy may be lower than the value obtained. This suggests that the dissociation of hydrogen from H_2O easily occurs on the aluminum surface.

3.2 Absorptions from perfect clean surface

The potential curves for hydrogen absorption through the perfect clean surface are shown in Figs. 12 and 13 as a function of the perpendicular distance from the surface. In these figures, the energy at each adsorption site is set at zero. The broken curve in Fig. 12 shows the result on the (100) model surface (Model 2). An adsorption point exists near the surface. However there is no stable point inside the cluster. This is due to a rapid instabilization caused by the repulsion with the second layer atom. The full curve in Fig. 12 shows the result on the (111) tetrahedral path (Model 3). It is found that there are an adsorption point around 1.0 Å outside the surface and a metastable point, which is very shallow (about 0.06 eV), around 0.6 Å under the surface. The inside point corresponds to just the tetrahedral site and is more instable than the outside minimum. In this case, there is a potential barrier of about 1.0 eV from the outside to the inside, unlike Model 2. This barrier may be caused by narrowing the gate, and therefore it should be lowered a little by considering the lattice relaxation. The result on the (111) octahedral path (Model 4) is shown in Fig. 13. There is an adsorption point at around 1.0 Å outside the surface as in the case of the tetrahedral path. The metastable points also exist between the surface and the second layer and between the second and the third layers. These inside minimum points correspond to the octahedral and tetrahedral sites, respectively. However, the height of the potential barrier from the outside to the inside is of about 0.5 eV, a half the value obtained for the tetrahedral path (Model 3). Thus it is considered that the repulsion between hydrogen and the second layer atom is weaker than the case of Model 3. The well at the tetrahedral site is deeper than the case of Model 3. In the bulk, the tetrahedral site may be more stable site. Moreover, it should be noticed that the octahedral site is about 0.7 eV more stable than the adsorption site near the surface site. The previous theoretical calculations by using the other methods have investigated that no internal

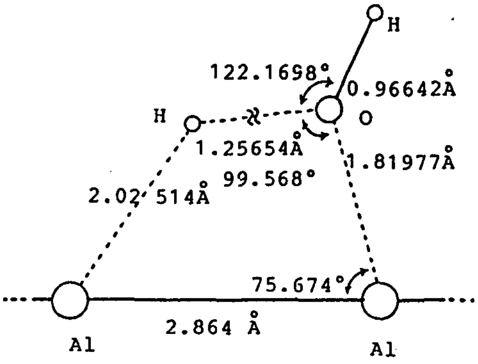


Figure 11 :

Transition State of Linear Al_4/H_2O.

Figure 12 →

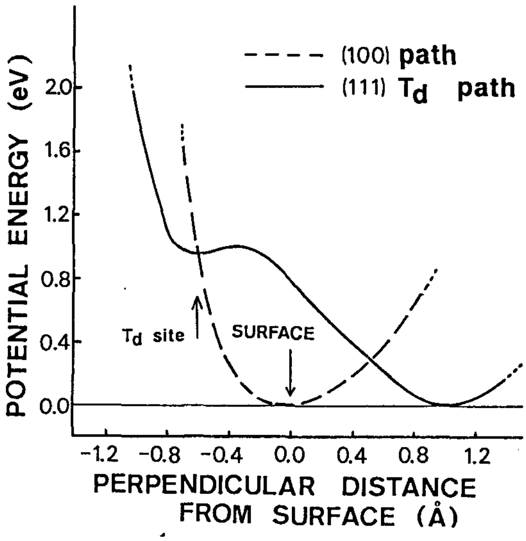
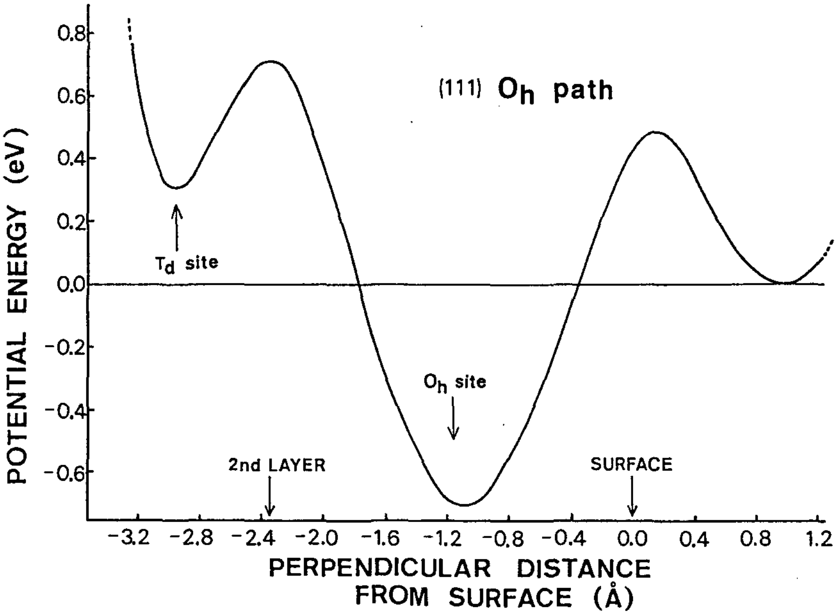


Figure 13 ↓



site is more stable than the surface site in perfect crystal. [5,6] However our result suggests the possibility which the more stable internal site than the surface site exists in the octahedral site between the surface and the second layer (the first octahedral site).

The net charge of hydrogen obtained is shown in Fig. 14 as a function of perpendicular distance from surface. Take notice to the change of the scale in the left-hand side from -1.2 Å in the horizontal axis. The dotted, broken and full curves indicate the results for the (100) path, the (111) tetrahedral path and the (111) octahedral path, respectively. The charge increases rapidly as hydrogen approaches to the surface, and becomes roughly constant inside the clusters though fluctuates a little. It is about -0.67e under the surface and is about -0.5e even at 0.8 Å outside the surface. Our results are far larger than the previous values of about -0.1e. [3-5] In this work, a 3-21G basis set which is split valence orbitals was used. So the wave functions of hydrogen have more degree of freedom than a minimal basis set. Therefore, it is considered that hydrogen can hold more electrons. However this results should be confirmed by using better basis set and by involving the electron correlations.

3.3 Absorption from distorted surface.

The potential curve for hydrogen absorption through the distorted gate (Model 5) is shown in Fig. 15, where the energy at the minimum point is set as the reference energy. An adsorption point exists near the surface as in the case of perfect surface mentioned above, however, in this case, there is no conspicuous potential barrier between the outside and the inside. The energy at the point 0.4 Å under the surface is only 0.1 eV higher than that at the adsorption point. When the dislocation through the surface is considered, the distorted gates continue from the surface to the depth. Therefore hydrogen may be absorbed easily along the dislocation line. This result supports an important role of defects introduced by the mechanical removal of the surface.

3.4 Absorption from surface with oxygen

After the dissociation of hydrogen from H_2O, OH is adsorbed at the hollow site. This was confirmed by the geometry optimization of OH-aluminum cluster. Because the dissociated hydrogen has large negative charge, it will strongly repel with negative oxygen and will be away from each other when the density of oxygen on the surface is low. However when the density becomes higher, the condition which there are hydrogen and oxygen closely may occur. Thus, in order to study the effect of oxygen near the hydrogen path, the potential curves were obtained using Models 6 and 7. The results are shown in Fig. 16, where the minimum energy site is set at zero. The broken and full curves show the results for the case with OH and the case with O at the hollow site adjacent to the hydrogen path, respectively. In both cases, it is found that the energies at the inside become lower than that on the surface. This is due to an instabilization of hydrogen on the surface by the existence of oxygen. Therefore, it is suggested that oxygen promotes the absorption of hydrogen at the early stage of the oxidation of the clean surface.

4.Conclusion

In this work, the activation energy for dissociation of hydrogen from H_2O on the aluminum surface and the potential energy curves for hydrogen

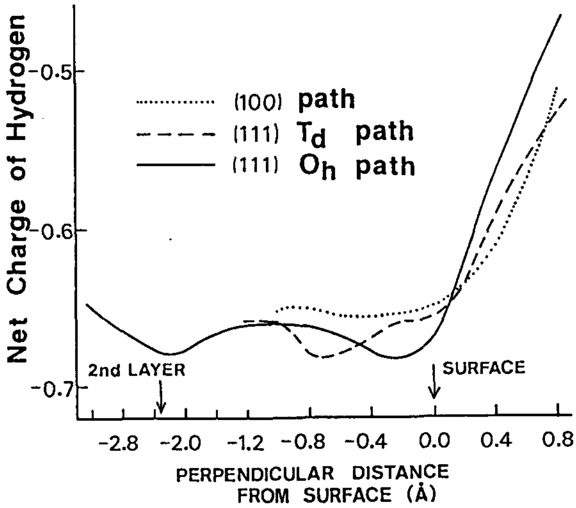


Figure 14

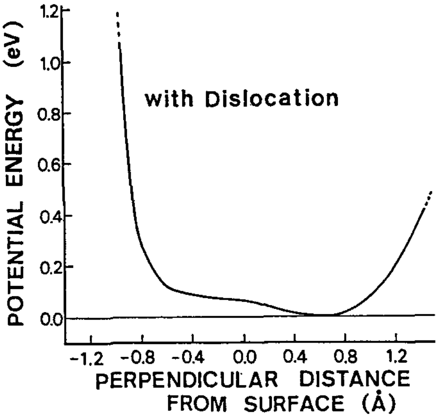


Figure 15

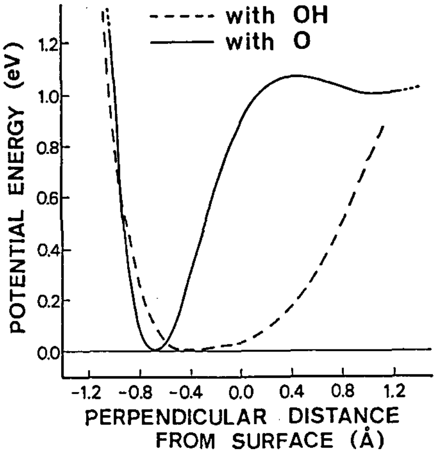


Figure 16

absorption into aluminum were obtained by ab initio molecular orbital method. The activation energy obtained is comparatively low. This suggests that hydrogen is supplied from H_2O by the reaction with aluminum on the clean surface. The results also support expectation that defects such as the dislocation through the surface play an important role on the absorption of hydrogen. Furthermore, it is suggested that the existence of oxygen on the surface promotes hydrogen absorption in the early stage of the oxidation of surface. Actually, both of them may affect in the same time.

However, larger cluster models and better basis set are still needed to obtain more qualitative and more reliable results. It is also important to consider the effect of vacancies. These improvements and attempts are currently under study.

Acknowledgements

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