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Molecular Orbital Study of Interfacial Strength between Silica Cluster and Polyimide Surface

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We investigated interfacial reactions between a silica cluster and a polyimide surface by the atomistic calculations combining with a semi-empirical molecular orbital method and the algorithms that can find minimum energy paths in the chemical reaction process. We demonstrated that chemical bonding occurs between a silica cluster and polyimide surface, and that the most probable reactions always involve bonding between a Si atom in the cluster and a carbonyl oxygen atom in the polyimide. Moreover, we discussed the interfacial strength of silica/polyimide substrate using the optimal minimum energy paths.

Key words: adsorption process, polyimide, zinc oxide cluster, minimum energy paths, sorption energy

1. INTRODUCTION

Understanding the bonding mechanisms of metal or ceramic oxide thin film/aromatic polyimide substrate interface is demanding in its applications for electronic devices, since chemical stability and mechanical integrity for such interfaces control authenticity of the devices [1,2]. Therefore, there are many researches according to properties of various interfaces such as copper/polyimide [2,3] and silicon/polyimide [4]. However, the evaluation method for the interfacial strength of oxide thin film/polymer substrate has not been proposed. Since the thickness of each component layer in such devices is generally less than one micron, atomic-level factors of adhesion and adsorption directly affect these interfacial properties.

An understanding of the chemical interactions at the interfaces has the potential to yield significant progress in the field of adhesion [5]. To discuss chemisorption at the interface, it is efficient to determine the minimum energy paths (MEPs) of the potential energy landscape. In general, it is difficult to predefine the MEPs, since the paths described in multi-dimensional space are usually complicated. Recently, Henkelman and Jónsson have proposed a dimer method [6] and a nudged elastic band (NEB) method [7,8] to find the MEPs. These methods are Hessian free in that they use only the first derivatives of the potential energy.

In the present study, to evaluate the strength of silica cluster/polyimide substrate interface, firstly, we investigate the MEPs for adsorption both by semi-empirical molecular orbital calculations and by the dimer and NEB methods. Secondary, we propose a method for evaluating ideal interfacial strength of the silica cluster/polyimide substrate system using the optimal minimum energy paths.

2. CALCULATION METHODOLOGIES

2.1 Total potential energy calculation

In order to obtain the potential energy landscape of the system, we utilize a semi-empirical molecular orbital method based on a PM5 Hamiltonian which is the latest revised version of PM3 [9] as coded in a general package MOPAC2002 [10,11].

2.2 The dimer method

The dimer method is used to search for the final, chemical reaction-induced state of a system. Let us consider a dimer constructed from two atomic images of a system. The dimer has a midpoint represented by a given configuration $\mathbf{R}$. If the system has n atoms, $\mathbf{R}$ is defined in $3n$ dimensional coordinate system. Two atomic images are displaced with a small distance ΔR from the midpoint of the dimer:

$$\mathbf{R}_i = \mathbf{R} \pm \Delta R\mathbf{N} \qquad (i = 1,2) \tag{1}$$

where the vector $\mathbf{N}$, which defines the dimer orientation, is a unit vector. The first part of the algorism is a dimer rotation. If the dimer does not lie on one of the MEPs, a certain torque around the midpoint **R** will act on the dimer to rotate the dimer to the lowest curvature direction. A modified Newton's method [6] is used to minimize the rotational torque. The second part of the algorithm is the translation of the dimer. In order to converge to a saddle point, the midpoint of the dimer is moved up the potential energy surface along the lowest curvature direction only, and down along the other ones. This movement is accomplished by the effective force given by the following equation:

$$\mathbf{F}_{eff} = \begin{cases} -\mathbf{F}^{\parallel} & C > 0 \\ \mathbf{F}_{\mathbf{R}} - 2\mathbf{F}^{\parallel} & C < 0 \end{cases} \tag{2}$$

where $\mathbf{F}_\mathbf{R}$, is the net translation force acting on the midpoint of the dimer; it comprises the average of the forces acting on each of the images. The variables $\mathbf{F}^{\parallel}$ and C are the forces acting, respectively, along the dimer orientation and along the curvature of the potential. After each translation, the dimer is reoriented and moved along the path. We employ an algorithm combining the conjugate gradient and the quick-min [6] methods (optimizing algorithm) in order to minimize $\mathbf{F}_\mathbf{R}$. Once the dimer reaches the saddle point, we move it a small distance along the path to the opposite side of the saddle point. Then, we minimize $\mathbf{F}_\mathbf{R}$ acting on the midpoint of the dimer by an optimizing algorism.

2.3 The NEB method

In the NEB method, an elastic band consisting of N+1 images [$\mathbf{R}_0$, $\mathbf{R}_1$, $\mathbf{R}_2$, …, $\mathbf{R}_N$] connected by springs is used for searching the MEPs; here, $\mathbf{R}_0$ and $\mathbf{R}_N$ are fixed at the local minima of the initial and final states. If the final state is not known, the dimer method can be used to find it. The N-1 intermediate images are adjusted by an optimization algorithm. The total force acting on an image is the sum of two kinds of forces which are the spring force along the local tangent and the true force perpendicular to the local tangent:

$$\mathbf{F}_i = \mathbf{F}_i^s|_{\parallel} - \nabla E(\mathbf{R}_i)|_{\perp} \qquad (i = 1, 2, \ldots, N+1) \tag{3}$$

where i is the index of the image, and $E(\mathbf{R}_i)$ is the total potential energy of image i. The true force, which is a part of Eqn. (3), is given by:

$$\nabla E(\mathbf{R}_i)|_{\perp} = \nabla E(\mathbf{R}_i) - \left(\nabla E(\mathbf{R}_i) \cdot \hat{u}_i\right)\hat{u}_i \tag{4}$$

where $\hat{u}_i$ is the normalized local tangent at image i. The spring force is given by:

$$\mathbf{F}_i^s|_{\parallel} = k\left(|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|\right)\hat{u}_i \tag{5}$$

where k is the spring constant. In order to move the images according to the force indicated by Eqn. (3), we again use an optimizing algorithm. The climbing image NEB method and variable spring constants are used to obtain the precise MEPs [7].

2.4 Modeling of the silica cluster/polyimide interface

As a polyimide substrate, we use a rod-like poly-(p-phenylene pyromellitimide). The relaxed atomic configuration of one repeating unit of polyimide is shown in Fig. 1. The initial molecular configuration of the repeating unit was determined using the X-ray structure analysis data [12]. To model the polyimide crystalline surface layer, we stack two polyimide molecular chains in the z direction as shown in Fig. 1. The lower polyimide layer is fixed. We employ a silica cluster with two Si and four O atoms as an adsorbate. The atomic configurations of the Si_2O_4 cluster and polyimide substrate are relaxed separately. Since there may exist the initial position dependency of the cluster, we place the relaxed Si_2O_4 cluster in 25 different positions in the x-y plane with an average distance Δz of 4.7Å above the polyimide surface. Periodic boundary conditions are set in the x and y directions. To obtain the metastable atomic configuration which is the initial state of the dimer method, we relax the atomic structures of the 25 systems.

2.5 Sorption energy

Figure 2 shows a schematic illustration of the adsorption process that takes place on the interface. The abscissa in Fig. 2 is the reaction coordinate S(**R**), a

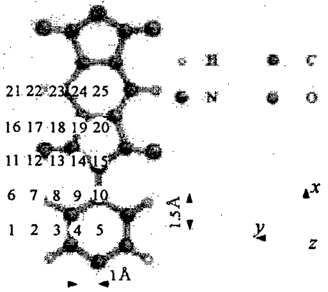

Fig. 1 Relaxed atomic configuration of one repeating unit of polyimide, and initial location points of the silica cluster above the polyimide surface.

normalized norm of the reaction path. Thus, the adsorption process is represented by the relation between the total energy $E(S)$ of the system and the reaction coordinate. We can describe the physisorption energy (ΔE_p) as the difference between the energy of the metastable state (E_t) and the sum of the energies of the isolated cluster (E_a) and the substrate (E_s). The activation energy is given by the difference between the energies of the transition state (E_{sad}) and E_t. The chemisorption energy (ΔE_c) is expressed by difference between the energies of final state (E_f) and E_t. We can evaluate $\Delta E_p+\Delta E_c$ as the total sorption energy.

2.6 Interfacial strength of silica cluster/polyimide substrate

We investigate the sum of z-axis directional forces acting on the cluster along the each MEPs as the interfacial force F_{INT} (Fig.3). We calculate the maximum interfacial force F_{INT}^{max} which is needed to dissociate the cluster from the polyimide substrate along the MEPs. The F_{INT}^{max} can be used as an index for evaluating the interfacial strength. We employ the area of one repeating unit of polyimide as the effective area A_{eff}. A interfacial strength S_{INT} of silica cluster/polyimide substrate can be then given by the following equation:

$$S_{INT} = F_{INT}^{max} / A_{eff} . \qquad (6)$$

3. RESULTS AND DISCUSSION

3.1 Adsorption process of the silica cluster/polyimide interface

Through the dimer method, we found that the silica cluster/polyimide systems starting from numbers 1, 2, 6, 8, 10, 12, 16 and 21 as shown in Fig. 1 converged to more stable states than the initial states entering by the saddle point. Therefore, we may confirm that a chemical reaction occurs between the silica cluster and the polyimide substrate. The other systems converged to states, in which the energies of the final state (E_f) were higher than those of the initial state (E_t). Using the initial and final atomic configurations, we performed an analysis using NEB method to get the precise MEPs of the system. Figure 4 shows the MEPs of the system with a chemical reaction. We calculated the activation, chemisorption and sorption energies from the MEPs, and brought these results together in Fig. 5, which also contains the atomic configurations of the metastable, transition and stable states. Systems 1, 2, 6, 12 and 16 must have a high activation energy due to a rupture of the C-N bond in the polyimide substrate indicated by an arrow as shown in Fig. 5(a). On the other hand, in systems 8 and 10, we see no such break. In system 8, the Si atom of the cluster and the carbonyl O atom in the diamine part of polyimide make covalent bonds, and the cluster forms a bridge between coadjacent molecular chains. In system 10, the silica cluster bridges the two diamine parts. The Si-O bonds in

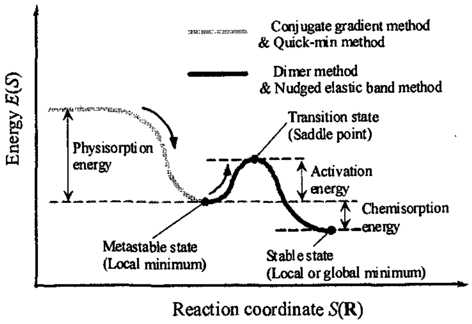

Fig. 2 Schematic illustration of the adsorption process at the silica cluster/crystal polyimide interface.

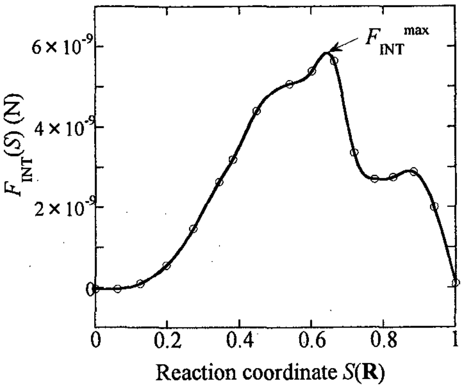

Fig. 3 Relation between F_{INT} and reaction coordinate of silica cluster/polyimide substrate system 3.

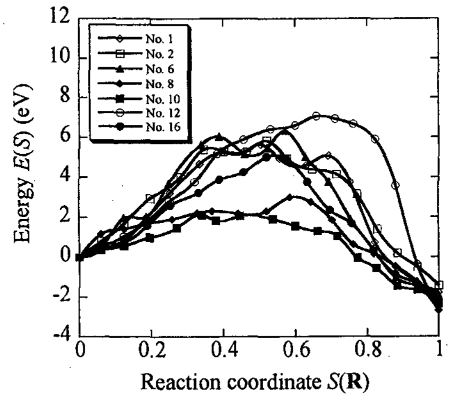

Fig. 4 MEPs obtained with the NEB method for silica cluster polyimide substrate systems.

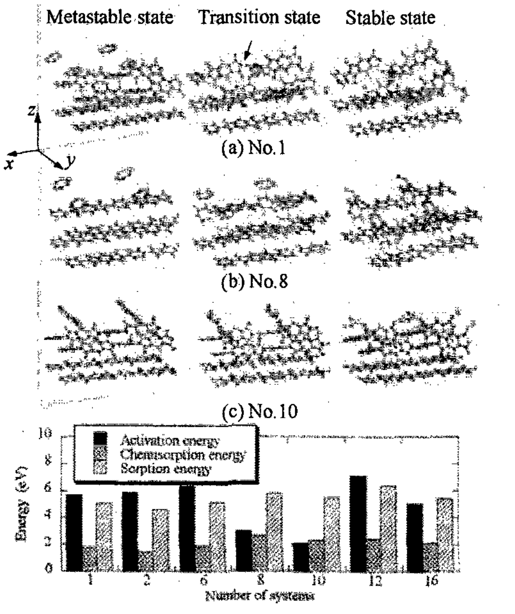

Fig. 5 (a)-(c) Atomic configurations of the metastable, transition and stable states in the adsorption process at the silica cluster/polyimide interface. (d) Activation, chemisorption and sorption energies of the silica cluster/polyimide systems per repeating unit of polyimide. Atomic configurations are shown by repeating the unit cell twice in each *x*, *y* direction.

Table I Peel strength of the surface layer of substrate and interfacial strength of silica/polyimide substrate systems 8 and 10.

	Polyimide	No. 8	No. 10
Strength (GPa)	10.71	2.64	9.44

both systems 8 and 10 makes the activation energy lower and the chemisorption energy higher. Therefore, Si-O bonding, as in systems 8 and 10, is likely to be the most probable of the reactions in the adsorption processes of the silica cluster/polyimide substrate, and to lead to a higher chemical stability.

3.2 Strength of the silica cluster/polyimide interface

We calculated the interfacial strength S_{INT} of systems 8 and 10 which indicated the probable reaction paths. Since two silica clusters can adsorb to one repeating unit of polyimide molecular chain, we used the duplicated S_{INT} as the interfacial strength. We also calculated a peel force of the polyimide surface layer having no cluster (F_p), which is needed to pull rigidly away the surface layer of polyimide from the substrate in the *z*-axis direction. A peel strength of the surface layer of substrate can be then defined by F_p/A_{eff}. We brought these results together in Table I. Type of reactions 8 and 10 occurs in almost the same probability, because the activation energies of systems 8 and 10 show almost the same values. Therefore, the average interfacial strength between silica and polyimide surface is around 6GPa which is about 60% of the peel strength of polyimide surface layer. Hence, we suppose that the failure occurs at the interface between the silica and the polyimide substrate.

4. CONCLUSIONS

In this study, we employed semi-empirical molecular orbital calculations to investigate the adsorption processes of a silica cluster and a polyimide substrate interface, and discussed the interfacial strength of silica/polyimide substrate using the optimal minimum energy paths. Of all of the reactions studied here, we found that the reactions involving a bonding between Si atom in the cluster and a carbonyl oxygen in the polyimide were the most likely to take place. Therefore, we believe that increasing the number of carbonyl groups in a unit surface area stabilizes the silica thin film/polyimide interface.

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