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Investigation of Bonding Energy of Morse Potential Energy of Silicon Substrate Dipped in Room Temperature Slurry

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Keywords: specific down force energy (SDFE), atomic force microscopy (AFM), single-crystal silicon substrate, bonding energy of Morse potential energy, room temperature slurry

ABSTRACT

The study uses specific down force energy (SDFE) theory and the theoretical model for calculation of the thickness of chemical reaction layer, and then establish the calculation method of bonding energy D value of Morse potential energy of the single-crystal silicon affected by chemical reaction of room-temperature slurry. The study uses a smaller down force and a cutting depth within the range of thickness of chemical reaction layer to calculate the bonding energy D value of Morse potential energy of the single-crystal silicon affected by room-temperature slurry. Finally, the study uses molecular statics nanocutting model and the obtained bonding energy D value of Morse potential energy of the single-crystal silicon affected by room-temperature slurry to simulate the cutting force and down force for cutting of single-crystal silicon substrate, and then compare the simulated cutting force and down force with those under the effects of room-temperature slurry obtained from calculation by SDFE method, so as to prove the acquired bonding energy D value of Morse potential energy affected by room-temperature slurry is reasonable.

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INTRODUCTION

Nanjo et al. (2003) treated the sharp tip of TM-AFM probe as a perfect sphere to carry out simulated small-sphere scanning on an ideal plate under a fixed setpoint value. Fang et al. (2000) used AFM probe to conduct a nano-scratching experiment of crystal-free silicon substrate coated with aluminum film. Experimental results showed that scratch depth deepened with the increase of probe load and scribing cycles. Wang et al. (2010) used AFM to cut nanochannel on silicon oxide surface, and explored through experiment how normal force was related to cutting speed and cutting depth. Yan et al. (2007) directly used AFM to construct a sort of computer numerical control (CNC) machining system, and took AFM probe as a cutting tool to carry out scratching of nanostructure on the silicon surface with copper film deposited. Lin and Hsu (2012) proposed using AFM and specific down force energy (SDFE) method to analyze the minimum cutting times for cutting of sapphire substrate up to a certain depth. Lin et al. (2015) used AFM and SDFE method to induce the down force and cutting force for cutting V-shaped groove.

Preston (1990) proposed the first theoretical model of material removal rate for CMP, and indicated that MRR=KPV, where MRR was material removal rate; P was pressure applied; V was relative speed of wafer to polishing pad; and K was Preston constant. Liu et al. (1996), taking statistical method and elastic theory as the foundation, induced a wear mechanism mode of wafer surface, and indicated that this mode was related to pressure, relative speed, nature of polishing particles, and the nature of the material of the polished object. And the removal rate was related to the polishing particles in slurry and the elastic modulus of the material on wafer surface.

Molecular mechanics was first developed in 1950 by Irving and Kirkwood (1950). The method used by the scholars, who used Newton's equation developed from his law of motion, was called molecular dynamics (MD). And the method used by the scholars who used energy minimization method was called molecular statics (MS). Its purpose was to find out the displaced position of each molecule of the object in accordance with the action force borne by the

molecules in the system and the initial position conditions. Nevertheless, since the time step of molecular dynamics was taken too small, the simulation process had to spend a lot of calculation time, thus causing a problem of difficult calculation. But if the time step value of the simulation was taken too great, there might be a problem that the value of sliding speed would be taken too great, and this would not meet the actual physical phenomenon. Then gradually, there were scholars using molecular statics method to simulate nanoscale studies, hoping to correct the problems encountered by molecular dynamics. Jeng and Tan (2004) took the principle of combination of molecular statics method and the smallest energy in finite element, as a framework to simulate the displacement and deformation process of nanoindentation. Hu et al. (1998) and Saraev et al. (1999) employed molecular statics, which did not consider time factor at all, to solve the problem of crack on material. Using this method, dynamic cracking behavior could be solved by statics method so as to overcome the limitation of time. Lin and Huang (2013) considered conducting two-dimensional cutting of copper material. They used Morse potential energy of copper as well as X- and Y-direction components of two-dimensional molecular statics to establish simultaneous equations of force balance, and also used Newton-Raphson method to solve the most suitable displaced position of new balance in multiple solutions. Finally, the total energy of the system's minimum potential energy was taken as the criterion to determine whether the general system had reached a balance.

In the existing literature, only the related parameters of Morse potential energy equation of single-crystal silicon and bonding energy values without considering the effect of chemical reaction of slurry could be checked. But during CMP of single-crystal silicon material, since the chemical reaction occurred in dipping of single-crystal silicon in room-temperature slurry would soften the material, the bonding energy value of Morse potential energy on the chemical reaction layer of the single-crystal silicon would be affected. However, the abovementioned literature did not explore the abovementioned the bonding energy value at all. Therefore, the study develops the method of calculating the bonding energy of Morse potential energy of single-crystal silicon dipped in room-temperature slurry.

EXPERIMENTAL EQUIPMENT AND DOWNWARD FORCE MEASUREMENT METHOD

Experimental Equipment and Materials

The study uses the diamond-coated probe of AFM as the cutting tool to conduct experiment of straight-line groove cutting on single-crystal silicon substrate, and makes observation. The study also uses AFM equipment to carry out nanocutting and measure the surface morphology of silicon substrate before and after cutting.

The slurry used by the study is colloidal silica suspension (pH value 9.6, volume concentration 50%) produced by Allied High Tech. Products. Inc., and is applicable to CMP experiment of single-crystal silicon substrate. The study used the Dimension 3100 (D3100) AFM machine of Veeco Digital Instruments Inc. equipped at the nano-laboratory of Tungnan University. The study takes single-crystal silicon substrate as the material of experiments. The material of single-crystal silicon substrate is at diameter 2 inches, and thickness 254-304μm.

The cutting tool of probe used in experiments is DT-NCHR diamond-coated probe produced by Nanosensors Inc. The thickness of the diamond coating is around 100 nm. The probe tip is a semi-sphere, something like a sphere, at a radius of around 150 nm. Therefore, when cutting single-crystal silicon substrate by this probe, the probe tip is similar to a semi-spherical cutting tool.

The spring constant provided by the manufacturer is 42 N/m, and the resonance frequency is 320 kHz. In order to obtain a more accurate spring constant k_r of probe, the AFM of Tapping Mode is used, and then the actual resonance frequency f_r of the probe for experiment can be found. Using the natural frequency equation of vibrational science, it can be known that the square of the resonance frequency of probe is positively proportional to the spring constant of the cantilever of probe. As a result, the spring constant of probe is $k_r = (f_r^2 \times k_v)/f_v^2$. Therefore, the actual spring constant k_r of the probe for experiments of the paper can be calculated and acquired from the resonance frequency f_v of the probe and the spring constant k_v of probe provided by the manufacturer, as well as the actually measured resonance frequency f_r (Lin and Hsu 2012). The resonance frequencies and the spring constants of probe used in experiments are shown in Table 1.

Table 1 Resonance frequencies and spring constants of probe used in experiments

f_r (resonance frequency measured by machine)	385 kHz	k_r (actual spring constant of probe)	60.8 N/m
f_v (resonance frequency provided by manufacturer)	320 kHz	k_v (spring constant of probe provided by manufacturer)	42.0 N/m

Measurement Method of Downward Force of AFM Probe

Focusing on the measurement way of downward force of probe on the workpiece to be cutted, the paper uses a force-distance curve for measurement. In accordance with the description on Dimension 3100 Manual of Veeco Digital Instruments Inc. (2000), through change of setting of the setpoint value, it can adjust the feedback circuit with cantilever deflected

and voltage maintained. Under the force calibration mode, the setpoint is the horizontal midline of force-distance curve. After setting of setpoint, the cantilever displacement value (d) of the downward force on the probe can be acquired. After multiplying this d value by the spring constant k_r of probe, downward force F_d can be obtained as follows:

$$F_d=k_rd \quad (1)$$

THEORETICAL MODEL AND EXPERIMENTAL METHOD OF SDFE

The SDFE of the study is defined as the product after multiplying the cutting depth by the downward force applied by the cutting tool of probe on workpiece. Which is the energy produced in the cutting process, then using the produced energy divides the volume removed from workpiece by cutting tool of probe, and expressed as equation (2) as follows (Lin and Hsu 2012):

$$\text{SDFE(specific down force energy)} = \frac{F_d \times \Delta d}{\Delta V} \quad (2)$$

where F_d denotes the downward force that the cutting tool applies on workpiece; Δd denotes the cutting depth, and ΔV denotes the workpiece volume removed by cutting tool of probe.

As known from the geometric relationshipin the contact between cutting tool and workpiece, the initial volume removal equation of the cutting tool that conducts downward force is:

$$\Delta V_1 = \pi \Delta d_1^2 \left(R - \frac{\Delta d_1}{3} \right) \quad (3)$$

where R denotes the radius of the cutting tool of probe tip; and Δd_1 denotes the cutting depth. After the cutting tool moves, the depth of the middle area of the cutted groove gradually inclines to be a fixed cutting depth. As for the removal volume by downward force the probe after the cutting tool moves, since the above cutting process is done, the volume of the distance of the radius R behind the cap of workpiece being cutted by the probe in advancing direction has been removed. Therefore, the removed volume at this moment is half of the volume of the spherical cap at the cutting depth. The removed volume is as follows:

$$\Delta V_1 = \frac{1}{2} \pi \Delta d_1^2 \left(R - \frac{\Delta d_1}{3} \right) \quad (4)$$

where R denotes the radius of the cutting tool of probe tip; and d_1 denotes the cutting depth of the 1st cutting pass.

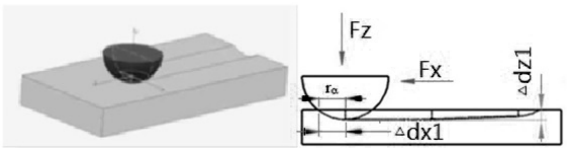

Fig.1. Schematic diagrams of forces of F_X and F_z , and Δd_{z1} and Δd_{x1} of different axles on V-shaped groove after the 1st cutting pass of nanocutting by AFM probe

Figure 1 shows the forces of F_X and F_z , and Δd_{z1} and Δd_{x1} on nanoscale V-shaped groove cut by AFM probe. The study lets the SDFE values of different axles during nanocutting of V-shaped groove on single-crystal silicon be the same fixed value. Hence, the relationships among different axles are rearranged as the following equations (Lin et al. 2015):

$$\text{SDFE} = \frac{F_z \times \Delta dz_1}{\Delta V_1} = \frac{F_x \times \Delta dx_1}{\Delta V_1} \quad (5)$$

$$\text{downward force } F_z \text{ of Z axle} = \frac{\text{SDFE} \times \Delta V_1}{\Delta dz_1} \quad (6)$$

$$\text{cutting force } F_x \text{ of X axle} = \frac{F_z \times \Delta dz_1}{\Delta dx_1} = \frac{\text{SDFE} \times \Delta V_1}{\Delta dx_1} \quad (7)$$

Therefore, if the spherical radius of the tip of AFM probe is measured, and if Δdz_1 is known, equation (3) and equation (4) can be used to calculate the volume ΔV_1 removed by cutting tool only during down press and the volume ΔV_1 removed by cutting of V-shaped groove in the 1st cutting pass. Besides, the study lets the SDFE of different axles be the same numerical value, so that the paper can acquire from experiment the SDFE of different axles for nanocutting of V-shaped groove on single-crystal Si. Then, equations (6) and (7) are used to calculate the down force Fz and cutting force Fx for nanocutting of V-shaped groove on single-crystal Si.

CALCULATION MODEL AND EXPERIMENTAL METHOD OF SDFE VALUE PRODUCED FROM CHEMICAL REACTION OF SLURRY AND THICKNESS OF CHEMICAL REACTION LAYER

Since the chemical composition of slurry would produce chemical reaction on the surface of single-crystal silicon substrate, a chemical reaction layer of softer material would be formed on the surface of single-crystal silicon substrate. Thus, the SDFE value of the single-crystal silicon affected by chemical reaction of room-temperature slurry is different from the SDFE value of the single-crystal silicon without considering the effects of chemical reaction of slurry. The study uses the slurry at volume concentration 50%. Single-crystal silicon substrate is dipped in room-temperature slurry at 23°C for 30 minutes, and then a smaller down force is applied to conduct AFM experiment and achieve a cutting depth. Using a smaller down force to conduct AFM cutting experiment is to ensure that the cutting depth of probe would not exceed the thickness of chemical reaction layer affected by room-temperature slurry. Then the SDFE value at this time is the correct SDFE value ($\text{SDFE}_{\text{reaction}}$) of the chemical reaction layer of the single-crystal silicon substrate affected by room-

temperature slurry.

In the experiment that uses AFM probe to cut and machine single-crystal silicon substrate, a smaller down force can be used to achieve the SDFE value ($SDFE_{reaction}$) of the chemical reaction layer of the single-crystal silicon surface affected by room-temperature slurry; and a greater down force can be used to achieve the SDFE value ($SDFE_{total}$) of the thickness exceeding that of the chemical reaction layer on the surface of the single-crystal silicon. The study also conducts AFM experiment to obtain the SDFE value ($SDFE_0$) of the single-crystal silicon without being dipped in room-temperature slurry. Besides, a greater down force is used. At this time the cutting removal depth of AFM probe Δd_{total} would be greater than the thickness of the chemical reaction layer of the single-crystal silicon substrate $\Delta d_{reaction}$, as shown in Figure 2.

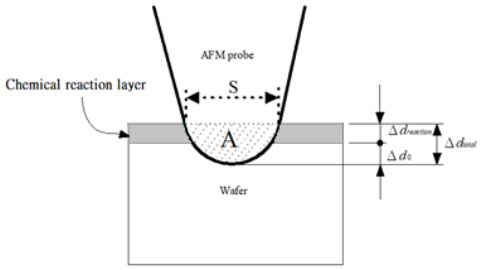

Fig.2. Schematic diagram of chemical reaction layer

If $\Delta V_0$is the removed volume of the cutting depth below the chemical reaction layer of the single-crystal silicon substrate Δd_0, the SDFE value of the single-crystal silicon substrate without being dipped in slurry will be $SDFE_0$. If the diameter of AFM probe and down force F_{aw} are known, it can be seen from Figure 2 that Δd_{total} can be known by measurement. Therefore, using equation (4), the cutting removal volume Δd_{total} can be acquired. In addition, from Figure 2, equation (8) can be obtained:

$$\Delta d_{total} = \Delta d_0 + \Delta d_{reaction} \quad (8)$$

Then, the total SDFE is ($F_{aw} \times \Delta d_{total}$). Using SDFE theoretical equation, the following is known:

$$F_{aw} \times \Delta d_{total} = F_{aw} \times (\Delta d_0 + \Delta d_{reaction}) = F_{aw} \times \Delta d_0 + F_{aw} \times \Delta d_{reaction} = SDFE_0 \times \Delta V_0 + SDFE_{reaction} \times \Delta V_{reaction} \quad (9)$$

Since $SDFE_0$ and ΔV_{total} can be known from calculation of the measurement data of AFM, and the SDFE value ($SDFE_{reaction}$) of the single-crystal silicon affected by the chemical reaction of slurry can be obtained from the abovementioned calculation method of the SDFE of the chemical reaction layer of the single-crystal silicon affected by the chemical reaction of slurry and from the AFM experiment.The removed volume of thickness of the chemical reaction layer of the single-crystal silicon substrate is $\Delta V_{reaction}$.

$$\Delta V_{reaction} = \Delta V_{total} - \Delta V_0 \quad (10)$$

From equation (9) and equation (10), the following equation can be induced:

$$\therefore \Delta V_0 = \frac{F_{aw} \times \Delta d_{total} - SDFE_{reaction} \times \Delta V_{total}}{SDFE_0 - SDFE_{reaction}} \quad (11)$$

For equation (4) $\Delta V_1 = \frac{1}{2}\pi \Delta d_1^2 \left(R - \frac{\Delta d_1}{3} \right)$, since it is known $\Delta V_0 = \Delta V_1$ and the probe tip radius is R, we can calculate equation (4) to achieve $\Delta d_0 = \Delta d_1$.

Furthermore, we can obtain

$$\Delta d_{reaction} = \Delta d_{total} - \Delta d_0 \quad (12)$$

As mentioned above, from the experiment, Δd_{total} can be measured, and Δd_0 can be obtained. Then, from equation (12), the thickness $\Delta d_{reaction}$ of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry can be calculated.

The study subsequently uses different down forces of AFM machine to control the cutting depth at an interval of 0.05nm when conducting AFM cutting experiment. When down force and cutting depth are increased, SDFE value starts to rise, implying that the down-press depth of probe has exceeded the thickness of the chemical reaction layer affected by slurry. Therefore, SDFE value starts to increase with the increase of down force and cutting depth. When SDFE value tends to become stable again, it implies that the probe has completely exceeded the thickness of the chemical reaction layer. Therefore, the SDFE value tends to become the SDFE value of the original material without being affected by slurry. Thus, it is determined that the range of thickness of the chemical reaction layer is the corresponding cutting depth after it exceeds the thickness of the chemical reaction layer and when SDFE value starts to change. In order to prove that the calculated result of thickness of the chemical reaction layer and the calculation equation are feasible, the study proposes to conduct the above AFM experiment first. The calculated thickness value of the chemical reaction layer of single-crystal silicon is taken as the main reference. Taking the cutting depths at an interval of around 0.01 nm and different down forces, the study conducts AFM straight-line cutting experiment of single-crystal silicon substrate, and further acquires the thickness of the chemical reaction layer from the experiment. The study compares the thickness value of the chemical reaction layer acquired from the experiment with the thickness value of the chemical reaction layer acquired from calculation in order to prove the accuracy and reliability in using the calculation method to obtain the thickness value of the chemical reaction layer of the single-crystal silicon substrate.

CALCULATION METHOD OF BONDING ENERGY OF MORSE POTENTIAL ENERGY OF SINGLE-CRYSTAL SILICON AFFECTED BY ROOM-TEMPERATURE SLURRY

Planning of Experiments and Planning of Research

Approaches

During CMP of single-crystal silicon, slurry is added, thus producing chemical reaction on the surface layer of the single-crystal silicon. As a result, the bonding energy between single-crystal silicon atoms weakens, and the material becomes soft, achieving a better removal effect during polishing. However, most of the literature explored the weakening of bonding energy between atoms used chemical reaction equation to explain its physical phenomenon, but did not explore the quantified numerical value for the chemical reaction layer to make the bonding energy of Morse potential energy of single-crystal silicon produce change. But for the bonding energy value of Morse potential energy of the single-crystal silicon after being dipped in room-temperature slurry, since the thickness of the chemical reaction layer of the single-crystal silicon dipped in slurry is usually very small, even smaller than 1 nm, the bonding energy cannot be easily measured. Therefore, there has been no exploration of this part in the related literature.

Molecular Statics Nanocutting Model

The lattice arrangement of the single-crystal silicon material explored in the study is to increase 4 atoms to FCC. The quasi-steady molecular statics nanocutting model of the study takes Morse potential energy of two-body potential energy as a reference for calculation of the action force of gravity or reaction force between molecules (Lin et al. 2014). Right now we have a great supposition in the simulation model of molecular statics cutting that the parameters and α for Morse potential energy of the single-crystal silicon within the thickness of chemical reaction layer for dipping in room-temperature slurry are unchanged, and only the bonding energy D value is changed. The main references are the parameters of balance distance between atoms (Å) and the material parameter ($Å^{-1}$) α, being a unit of size. The one with relation to the energy between Si-Si bonds of single-crystal silicon is the bonding energy D value only.

For the Morse potential used by the study, the gradient of Morse potential is taken as a negative number to find the action force between two atoms, as expressed in equation (13):

$$F(r_{ij}) = -\frac{\partial \Phi(r_{ij})}{\partial(r_{ij})} = 2D\alpha\left\{e^{-2\alpha(r_{ij}-r_0)} - e^{-\alpha(r_{ij}-r_0)}\right\} \quad (13)$$

When, the potential energy action tends to become zero. Thus, cutoff radius is set to be r_c. When the distance exceeds r_c, since the action force of Morse force between two atoms is very small, all of them will not be calculated. When, the action force between atoms is just situated at a balance between attraction and repulsion. The probe and workpiece are under the condition of no action force.

The action force of Morse force among atoms is expressed as equation (14):

$$\vec{F}_i = \sum_{i=1}^{n} \vec{F}_{ij}(r_{ij}) \quad (14)$$

where i denotes the code for diamond probe atom; j denotes the code for workpiece atom in workpiece; n denotes the quantity of workpiece atoms; and denotes the distance between two atoms.

After action force is obtained, cutoff radius method is used. Subsequently, calculate the action force between atoms.

$$\vec{F}_i = \sum_{i=1}^{n} \vec{F}_{ij}\,\delta(r_{ij}) \qquad \begin{array}{ll} if & r_{ij_c} \geq r_c \Rightarrow \delta = 0 \\ else & r_{ij} \leq r_c \Rightarrow \delta = 1 \end{array} \quad (15)$$

The numerical values of the produced action forces are the components of forces F_x, F_y and F_z of three axles, which are shown in equation (16):

$$\vec{F}_i = \vec{F}_{x_i} + \vec{F}_{y_i} + \vec{F}_{z_i} \quad (16)$$

where $\vec{F}_{x_i}$ denotes the force of component for action force in X direction; $\vec{F}_{y_i}$ denotes the force of component for action force in Y direction; and $\vec{F}_{z_i}$ denotes the force of component for action force in Z direction.

Then, it is further decomposed to be Morse force component in X direction (F_x), Morse component in Y direction (F_y) and Morse component in Z direction (F_z). Let each of them be 0, creating a force balance equation of the quasi-steady molecular statics nanocutting model. Adding up the action forces of three axles produced from n pieces of material atoms onto m pieces of probe atoms on cutting tool, the total force of three axles can be acquired. The total force in X direction, F_x is the cutting force produced during cutting by diamond probe; F_z is the down force during cutting by diamond probe; and F_y is the lateral force between diamond probe and workpiece.

The study uses Hooke-Jeeves pattern search method in direct search method to look for the most suitable displaced position of each step for reaching force balance. Since AFM diamond probe is taken by the study as the cutting tool for cutting single-crystal silicon, the paper has to consider the correlation between C atoms of diamond probe and single-crystal silicon workpiece. The si-si and si-c used by the study and the numerical values of Morse potential parameters between atoms are shown in Table 2. The bonding energy D value (3.032 ev) in Table 2 is the bonding energy value of Morse potential energy of single-crystal silicon without being dipped in slurry.

Table 2 Parameters of Morse potential energy for cutting of the single-crystal silicon, without being dipped in slurry, by the cutting tool of AFM diamond probe (Tang 2007) (Martin et al. 1986)

Method for Calculating the Bonding Energy D

	si-si	si-c
D: bonding energy (ev)	3.032	0.435
α: material parameter ($Å^{-1}$)	0.7981	4.6487
r_0: balance distance between atoms (Å)	4.208	1.9475

value of Morse Potential Energy of the Single-crystal Silicon Affected by Room-temperature Slurry

The study uses a fixed down-press depth, which is within the chemical reaction layer affected by slurry. Then the study uses AFM experiment and SDFE theory to calculate the SDFE value of the chemical reaction layer of the single-crystal silicon dipped in room-temperature slurry, and the down force for downward press to the fixed down-press depth. After that, the bonding energy D value in Morse potential energy of the single-crystal silicon without being dipped in slurry is taken as an initially guessed value. The initially guessed bonding energy value is D_0. After substituting D_0 in the molecular statics nanocutting model to simulate up to the same fixed down-press depth, the simulated initial down force is calculated. These two methods, SDFE method and the method of molecular statics nanocutting model, are used to calculate the difference of down force F_d, which is taken as the convergence function. The equation of the convergence function is expressed as equation :

$$\frac{|F_{dSDFE}-F_{dMS}|}{F_{dSDFE}} \leqq \varepsilon \qquad (20)$$

Here, F_{dSDFE} denotes the down force on the single-crystal silicon dipped in room-temperature slurry, as calculated by SDFE method and from the SDFE value of the chemical reaction layer of the single-crystal silicon dipped in room-temperature slurry; F_{dMS} denotes the down force calculated by molecular statics nanocutting model; and ε denotes the convergence value. Based on the difference between $\frac{|F_{dSDFE}-F_{dMS}|}{F_{dSDFE}}$ and convergence value ε, optimization method is used to step by step adjust the bonding energy D value of Morse potential energy. When the value of $\frac{|F_{dSDFE}-F_{dMS}|}{F_{dSDFE}}$ converges to below ε, the bonding energy D value obtained at this moment is the bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon dipped in room-temperature slurry. Finally, the study uses the calculated bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate affected by dipping of it in room-temperature slurry. A smaller probe radius size is adopted. Molecular statics nanocutting model is used to simulate the cutting force and down force for cutting of a whole piece of single-crystal silicon material, which is supposed to be affected by dipping of it in room-temperature slurry. The obtained results are compared with the cutting force and down force acquired from calculation by SDFE value of the chemical reaction layer of the single-crystal silicon affected by dipping of it in room-temperature slurry, so as to prove that the acquired bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon affected by room-temperature slurry is reasonable.

RESULTS AND DISCUSSION

SDFE of Single-crystal Silicon Without Being Dipped in Slurry

We used different down force as 32.79μN, 38.5μN and 47.31μN to make the AFM experiment and obtain the cutting depths. Then using SDFE equation for calculation, the average SDFE value ($SDFE_0$) of the single-crystal silicon without being dipped in slurry is found to be 0.01775($^{\mu N \cdot nm}/_{nm^3}$)

$SDFE_{reaction}$ Value of Single-crystal Silicon Substrate Dipped in Room Temperature Slurry

Table 3 shows the AFM experimental results of different down forces in the chemical reaction layer of the single-crystal silicon substrate being dipped in slurry (volume concentration 50%) under room temperature 23°C for 30 minutes, and the calculated $SDFE_{reaction}$ value for dipping in room-temperature slurry. From Table 3, we can see that the average value of $SDFE_{reaction}$ value in the chemical reaction layer is 0.016208($^{\mu N \cdot nm}/_{nm^3}$).

Table 3 Down forces, cutting depths and removed volumes for the 1st pass of straight-line machining on the single-crystal silicon substrate dipped in slurry for 30 mintues, and SDFE values ($SDFE_{reaction}$) of the chemical reaction layer affected by slurry (slurry : volume concentration 50%, temperature 23 °C)

Down force in experiment F (μN)	Cutting depth Δd_{Z1}(nm)	Removed volume $\Delta V_1(nm^3)$	$SDFE_{reaction}$ ($^{\mu N \cdot nm}/_{nm^3}$)
0.31	0.081	1.54562	0.016208
0.32	0.084	1.66222	0.016208
0.34	0.089	1.86597	0.016208
0.36	0.093	2.03745	0.016208
Average value of $SDFE_{reaction}$			0.016208

Experimental and Calculation Results of the Thickness of Chemical Reaction Layer of Slurry Dipped in Room-temperature Slurry

The study firstly uses different down forces of AFM machine to control the cutting depth at an interval of 0.05nm when conducting AFM cutting experiment, as shown in the experimental results in Table 4. As indicated in Table 4, the interval of cutting depth is around 0.05 nm. In the first half of the experiment, the study uses a smaller down force, implying that cutting is performed within the range of chemical reaction layer affected by room-temperature slurry. Therefore, its SDFE value may be situated in a more stable condition. When down force and cutting

depth are increased, SDFE value starts to rise, implying that the down-press depth of probe has exceeded the thickness of the chemical reaction layer affected by slurry. Therefore, SDFE value starts to increase with the increase of down force and cutting depth.

Table 5 shows the application of Table 4's several greater down forces of the SDFE values exceeding that being dipped in room-temperature slurry. Using the equation for calculation of the thickness of chemical reaction layer, the thickness of chemical reaction layer $\Delta d_{reaction}$ is calculated to be 0.1481nm. Besides, as shown in Table 3, in the calculation of SDFE value of the single-crystal silicon dipped in room-temperature slurry, the maximum cutting depth Δd_{Z1} of the conducted AFM cutting is 0.093 nm, which is smaller than the thickness 0.148nm of chemical reaction layer, further proving that the SDFE value ($SDFE_{reaction}$) of the single-crystal silicon dipped in room-temperature slurry, acquired by the study, is reasonable.

Table 4 Down forces, cutting depths, removed volumes and SDFE values for AFM experiment of the single-crystal silicon substrate dipped in slurry for 30 minutes at an interval of 0.05 nm (slurry: volume concentration 50%, temperature 23℃)

Down force in experiment F(uN)	Δd_{total}(nm)	ΔV_{total} (nm^3)	$SDFE_Z$ ($\mu N \cdot nm/nm^3$)
0.18	0.046	0.4985	0.016208
0.35	0.092	1.9939	0.016208
0.57	0.148	5.15931	0.016208
0.77	0.196	9.04761	0.016657
0.97	0.245	14.1354	0.016773
1.18	0.298	20.9101	0.016802
1.38	0.347	28.3488	0.016935
1.58	0.394	36.5446	0.017047
1.81	0.443	46.1946	0.017327
2.04	0.496	57.9023	0.017495
2.28	0.549	70.9293	0.017681
2.47	0.594	83.0253	0.017693

As shown in Table 6, taking the cutting depths at an interval of around 0.01 nm and different down forces, the study conducts AFM straight-line cutting of single-crystal silicon substrate. As seen from the experiment, when down force reaches 0.57 uN, the thickness of chemical reaction layer of the experiment at this moment is 0.148 nm, and the SDFE value ($SDFE_{reaction}$) of this thickness of chemical reaction layer is 0.016208 ($\mu N \cdot nm/nm^3$). Right now, the SDFE value reaches a critical point. This is because when the down force is 0.59 uN, the cutting depth is 0.155 nm, and its SDFE value is 0.016226 ($\mu N \cdot nm/nm^3$), being greater than $SDFE_{reaction}$. Therefore, the thickness value of chemical reaction layer acquired from the experiment is 0.148 nm. Compare this result with the thickness of chemical reaction layer $\Delta d_{reaction}$ 0.1481 nm acquired from calculation in Table 5, it is proved that between the thickness value of the chemical reaction layer of single-crystal silicon substrate obtained by the calculation method and the thickness of the chemical reaction layer obtained from experiment, the difference in between is very small. Therefore, the thickness value of the chemical reaction layer of the single-crystal silicon substrate dipped in room-temperature slurry obtained by such calculation way is reasonable and acceptable.

Table 5 Calculated results of the thickness of chemical reaction layer of the single-crystal silicon substrate dipped in room-temperature slurry at 23°C obtained from the equation of chemical reaction layer thickness value (Average $\Delta d_{reaction} \fallingdotseq 0.1481$nm) (slurry: volume concentration 50%, dipping time 30 minutes)

Down force in experiment F(μN)	Δd_{total} (nm)	ΔV_{total} (nm^3)	F × Δd_{total}	$SDFE_{reaction}$ × ΔV_{total}	ΔV_0 (nm^3)	Δd_0(nm)	$\Delta d_{reaction}$ (nm)
0.77	0.196	9.04761	0.15092	0.146644	0.54281	0.048	0.148
1.18	0.298	20.91009	0.35164	0.338911	5.29261	0.1499	0.1481
1.38	0.347	28.34883	0.47886	0.459478	9.32664	0.199	0.148
1.58	0.394	36.5446	0.62252	0.592315	14.23937	0.2459	0.1481
				Average $\Delta d_{reaction} \fallingdotseq 0.1481$ nm			

Table 6 Down forces, cutting depths, removed volumes and SDFE values for AFM experiment of the single-crystal silicon substrate dipped in slurry for 30 minutes with cutting depth at an interval of 0.01 nm (slurry: volume concentration 50%, temperature 23°C)

Down force in experiment F(μN)	Δd_{total}(nm)	ΔV_{total}(nm^3)	$SDFE_Z$ ($\mu N \cdot nm/nm^3$)
0.32	0.084	1.66222	0.016208
0.36	0.093	2.03745	0.016208
0.41	0.107	2.69697	0.016208
0.45	0.119	3.33572	0.016208
0.49	0.128	3.85929	0.016208
0.52	0.136	4.35670	0.016208
0.57	0.148	5.15931	0.016208
0.59	0.155	5.65881	0.016226
0.63	0.164	6.33491	0.016387

Calculation Result of Bonding Energy D of Morse Potential Energy of the Single-crystal Silicon Affected by Room-temperature Slurry

The study uses the fixed down-press depth 0.14nm to calculate the bonding energy D value of Morse potential energy of the single-crystal silicon substrate affected by room-temperature slurry. Such a fixed down-press depth is within the range of thickness 0.148 nm of the chemical reaction layer affected by slurry. Then the study uses AFM experiment and SDFE theory to make calculation, and achieves that the down force for the down-press depth 0.14nm within the chemical reaction layer of the single-crystal silicon substrate dipped in room-temperature slurry is 6.962Nn (F_{dSDFES}). After that, the bonding energy of Morse potential energy of the single-crystal silicon without being dipped in slurry

D_0=3.032ev is taken as the initially guessed value. The study further supposes that D_0 is substituted in the molecular statics nanocutting model, and after simulating up to the same fixed down-press depth 0.14 nm, the study calculates the simulated initial down force (F_{dMS0}). Substitute the difference in down force F_d calculated by the abovementioned two methods in the convergence function equation. The convergence function equation is $\frac{|F_{dSDFES}-F_{dMS}|}{F_{dSDFES}} \leqq \varepsilon$. Figure 3 shows that the down force F_{dMS0} for simulation of molecular statics nanocutting model, with probe tip radius 2nm, down-press depth 0.14nm and D value 3.032ev, is 7.779 nN. As observed from the calculation results in Figure 5, when D_0=3.032ev (bonding energy of Morse potential energy of Si-Si not being dipped in slurry), as simulation has been up to the down-press depth 0.14 nm, the down force is F_{dMS0}=7.779nN, which is substituted in the equation $\frac{|F_{dSDFES}-F_{dMS}|}{F_{dSDFES}} \leqq \varepsilon$. After calculation, ε_0=0.1174 can be obtained. The study uses optimization method to step by step adjust the D value of Morse potential energy. First of all, the study uses a D value greater than D_0, and employs molecular statics nanocutting model to calculate the down force. Then the trend of change of its size can be observed. Therefore, D_1=3.2 ev is firstly substituted in the molecular statics nanocutting model to simulate the down force F_{dMS1}=8.432 nN under a fixed down-press depth 0.14nm. The down force is substituted in the convergence function equation $\frac{|F_{dSDFES}-F_{dMS}|}{F_{dSDFES}} \leqq \varepsilon$. After calculation, it is acquired that $\varepsilon_1 \fallingdotseq 0.2110$. After comparing ε_0 with ε_1, it is known that $\varepsilon_1 > \varepsilon_0$. Thus, the reasonable D value of Morse potential energy of the single-crystal silicon affected by room-temperature slurry should be smaller than the initially guessed value 3.032 ev. Therefore, the study adjusts the D value downwards. After that, D_2=2.95ev is substituted in the molecular statics nanocutting model. It is calculated that at a fixed down-press depth 0.14nm, the down force is F_{dms2}=7.526 nN, which is then substituted in the convergence function equation. After calculation, ε_2= 0.0810. Comparing ε_0=0.1174 with ε_2=0.0.0810, it is known that $\varepsilon_2 < \varepsilon_0$. Therefore, ε value has been step by step converging, indicating that the gradual downward adjustment of D value is correct. Thus, the study rearranges the calculation results of the simulated molecular statics nanocutting model and shows them in Table 7. As known from Table 7, the bonding energy D_0 value of Morse potential energy of the single-crystal silicon without being dipped in slurry is 3.032ev, under which the down force of the simulated molecular statics nanocutting model is 7.779 nN. After calculation, we acquire convergence value ε=0.117. Subsequently, the step-by-step downward adjusted bonding energy D value is substituted in the molecular statics nanocutting model to simulate calculation of its down force, and prove whether the convergence value ε is falling continuously. From Table 7, it can be seen that when bonding energy D value is 2.753ev, its down force F_{dMS} is 6.986 nN, and the convergence value ε=0.00345; and when the bonding energy D value is 2.748ev, the convergence value ε=0.00353. After making comparison, it is known that at this moment the convergence value of the downward adjusted bonding energy D value has begun to increase, and would not decrease. In order to confirm whether the bonding energy D value 2.753ev is a better value, the bonding energy D value 2.75ev is substituted in the molecular statics nanomachining model to simulate the down force, achieving the convergence value ε=0.0349. After comparing this convergence value with the convergence value ε=0.00345 with bonding energy D value being 2.753ev, it is known that the bonding energy D value 2.753ev is a better solution. Finally, the bonding energy D value 2.753ev is substituted in the molecular statics nanomachining model to simulate the down force so as to confirm whether the convergence value ε is increasing continuously. The achieved convergence value ε=0.00437. When the bonding energy D value is greater than 2.753ev, the convergence value ε=0.00345. It can be confirmed that when the bonding energy D value is smaller than 2.753ev, the convergence value ε starts to increase gradually. Therefore, 2.753ev can be taken as the bonding energy D value of Morse potential energy of the single-crystal silicon dipped in room-temperature slurry.

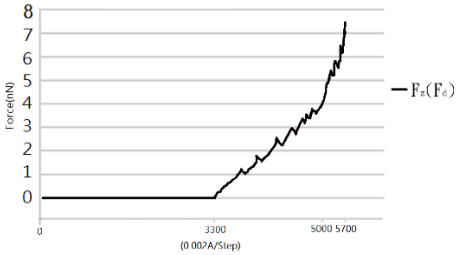

Fig.3. In the simulation of the molecular statics nanomachining model with probe tip radius 2nm, down-press depth 0.14nm and D_0 value 3.032ev, the down force F_{dMS_0} is 7.779 nN.

Table 7 Down forces and convergence values under different bonding energy D values obtained from simulated calculation with probe tip radius 2 nm and down-press depth 0.14 nm

Simulated parameters		Down force F_{dMS}(nN)	Convergence value (ε)
Down-press depth (nm)	Bonding energy D value (ev)		
0.14nm	3.2	8.432	0.211
0.14nm	3.032	7.779	0.1174
0.14nm	2.95	7.526	0.081
0.14nm	2.9	7.408	0.064
0.14nm	2.85	7.259	0.0426
0.14nm	2.80	7.151	0.0272
0.14nm	2.785	7.048	0.0123

0.14nm	2.775	7.013	0.0073
0.14nm	2.768	6.999	0.00434
0.14nm	2.763	6.992	0.00401
0.14nm	2.758	6.988	0.00372
0.14nm	2.753	6.986	0.00345
0.14nm	2.75	6.938	0.00349
0.14nm	2.748	6.937	0.00353
0.14nm	2.745	6.932	0.00437

Verification of the Bonding Energy D Value of Morse Potential Energy of the Chemical Reaction Layer of the Single-crystal Silicon Affected by Room-temperature Slurry

The study finally uses a probe with tip radius 2 nm, bonding D value 2.753ev of Morse potential energy, and molecular statics nanocutting model to simulate cutting of the single-crystal silicon within the range of thickness of chemical reaction layer affected by room-temperature slurry, and its cutting depth is 0.14nm. The cutting force value and the down force value, obtained from calculation by SDFE method, of the single-crystal silicon affected by room-temperature slurry are 1.3249 nN and 6.956 nN respectively. When the bonding energy D value of Morse potential energy of single-crystal silicon is 2.753ev, the average cutting force of the single-crystal silicon cut by the simulated molecular statics nanocutting model is 1.329 nN; and the average down force is 6.980nN, as shown in Figure 4. It can be observed that the average cutting force and average down force obtained from simulation are quite close to the cutting force and down force obtained from SDFE method. Therefore, it is proved that the bonding D value 2.753 ev of Morse potential energy of the chemical reaction layer of the single-crystal silicon affected by room-temperature slurry, as acquired by the study, is reasonable.

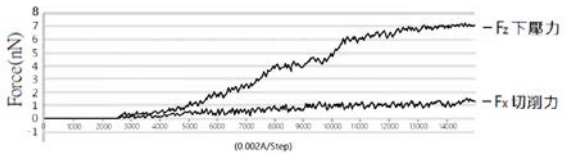

Fig.4. In the simulation of the molecular statics nanocutting model with probe tip radius 2nm, down-press depth 0.14nm and D value 2.753 ev, the average cutting force is 1.329 nN, and the average down force is 6.980 nN.

CONCLUSION

Focusing on the single-crystal silicon substrate affected by room-temperature slurry, the study innovatively proposes to conduct AFM experiment, use SDFE theory and the theoretical model for calculation of the thickness of chemical reaction layer, and then establish the calculation method of bonding energy D value of Morse potential energy of the single-crystal silicon affected by chemical reaction of room-temperature slurry. Using SDFE theory, the study acquires the SDFE value of the chemical reaction layer of the single-crystal silicon dipped in room-temperature slurry. The study also uses the theoretical model and experimental method for calculation of the thickness of chemical reaction layer of the slurry for dipping, to obtain the thickness of chemical reaction layer of the single-crystal silicon dipped in room-temperature slurry.

The study also uses molecular statics nanocutting model to simulate the down force application process of the single-crystal silicon dipped in room-temperature slurry at a fixed down-press depth. The main reason for using a fixed down-press depth to calculate the bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon dipped in room-temperature slurry is that we hope to shorten the calculation time required for simulation of the molecular statics nanocutting model. Therefore, a fixed down-press depth requiring less simulation time is selected to conduct simulation of down press of the molecular statics nanocutting model in order to more rapidly find the bonding energy D value of Morse potential energy of the single-crystal silicon affected by room-temperature slurry. Finally, the study uses the calculated bonding energy D value of Morse potential energy of the single-crystal silicon affected by room-temperature slurry, and uses molecular statics nanocutting model to simulate the average cutting force and average down force for cutting of the single-crystal silicon in the chemical reaction layer. The cutting force and down force are compared with the cutting force and down force of the single-crystal silicon affected by room-temperature slurry obtained from calculation by SDFE method, so as to prove that the acquired bonding energy D value of Morse potential energy of the single-crystal silicon affected by room-temperature slurry is reasonable.

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浸泡室溫研磨液之單晶矽基板的莫氏勢能結合能研究

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摘要

本文以比下壓能理論及計算化學反應層厚度理論模式，建立受室溫研磨液化學反應影響之單晶矽莫氏勢能之結合能D值的計算方法。本文先用較小的下壓力計算在化學反應層內所得受室溫研磨液影響之單晶矽莫氏勢能結合能D值。最後用所得之D值及分子靜力學奈米切削模式模擬切削具有受室溫研磨液影響的單晶矽基板的切削力與下壓力，並與比下壓能法計算所得之受室溫研磨液影響的切削力與下壓力作比較，以驗證所得之受室溫研磨液影響之莫氏勢能的結合能D值為合理。