中國機械工程學刊第四十一卷第三期第 253~263 頁(民國一百零九年)
Journal of the Chinese Society of Mechanical Engineers, Vol.41, No.3, pp 253~263 (2020)

Establishment and Analysis of Calculation Method of Bonding Energy of Morse Potential Energy of The Single-Crystal Silicon Affected by Its Being Dipped in Slurry at Different Temperatures

Zone-Ching Lin*and Bo-Tang Zhao **

Keywords: silicon, atomic force microscopy (AFM), specific down force energy (SDFE), bonding energy of Morse potential energy, thickness of chemical reaction layer, slurry temperature

ABSTRACT

Considering the affected by the different dipping slurry temperatures of the single-crystal silicon for the bonding energy values of Morse potential energy of single-crystal silicon, the paper uses specific down force energy (SDFE) theory and calculation method of theoretical model for calculation of the thickness of chemical reaction layer to calculate the bonding energy D value of Morse potential energy of the single-crystal silicon dipped in slurry at different temperatures. Then the paper uses molecular statics nanocutting model to simulate the cutting force and down force for cutting of single-crystal silicon, and then makes verification in order to understand the effects of different slurry temperatures on bonding energy. Finally, focusing on a fixed down force and using SDFE theory, the paper calculates the cutting depth of the single-crystal silicon substrate dipped in slurry at different temperatures, and explores the relationship between change of bonding energy for dipping in slurry at different temperatures and the cutting depth.

Paper Received March, 2020. Revised May,2020. Accepted June, 2020. Author for Correspondence: Zone-Ching Lin.
* *Professor, Department of Mechanical Engineering, National Taiwan University of Science and Technology, No.43, Keelung Rd., Sec.4, Da'an Dist., Taipei City 10607, Taiwan, email: zclin@mail.ntust.edu.tw.*
** *Graduated Student, Department of Mechanical Engineering, National Taiwan University of Science and Technology, No.43, Keelung Rd., Sec.4, Da'an Dist., Taipei City 10607, Taiwan, email: m10603217@mail.ntust.edu.tw*

INTRODUCTION

In the light of frequent application of chemical mechanical polishing (CMP) to the semiconductor industry, researches of CMP-related techniques and exploration of parameters are considered core technologies in the semiconductor industry. In CMP process, addition of slurry is often needed. The chemical reaction produced between slurry and silicon substrate can make the silicon substrate material within the thickness of chemical reaction layer become softened, and further enhance the grinding removal depth of silicon substrate per unit time during chemical mechanical polishing of silicon substrate.

Speaking of silicon substrate, when the material is softened because of chemical reaction of slurry, it implies that the bonding energy of Morse potential energy of silicon substrate would be weakened. However, according to the existing literatures, what can be found are only the parameters relating to Morse potential energy equation of single-crystal silicon substrate without chemical reaction of slurry, as well as the value of bonding energy. As to discussion relating to weakening of interatomic bonding energy, most of the literatures used chemical reaction equation to interpret the physical phenomenon; but the bonding energy value of Morse potential energy of the silicon substrate affected by chemical reaction of slurry at different temperatures is still not known yet.

Atomic force microscopy (AFM), invented by Bining et al. (1986), is a kind of scanning probe microscopy generally applied to measurement and observation of surface morphology of conductors and nonconductor. Therefore, related scholars made discussions on measurement and application of AFM. Nanjo et al. (2003) treated the tip of AFM probe as a perfect sphere to carry out simulated small-sphere

scanning on an ideal plate under a fixed setpoint value. It was proved by the related scholars that applying AFM probe as a machining tool to carry out mechanical cutting was a quite useful technique in machining of nanostructures, such as semiconductor, optoelectronic component and metallic surface (Tseng et al. 2008). Lin and Hsu (2012) proposed using AFM and specific down force energy (SDFE) method to analyze the minimum number of machining times for machining 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 a V-shaped groove.

Molecular mechanics was first developed 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. 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 et al. (2014) proposed three-dimensional quasi-steady molecular statics nanoscale cutting model to study the nanoscale orthogonal cutting of single-crystal silicon material having rows of atoms with vacancy defect.

In 1927 Preston (1927) proposed the first theoretical model of CMP wear, which was expressed as MRR=KPV, where MRR is material removal rate; P is the pressure applied; V is relative speed of wafer to polishing pad; and K is Preston constant. As seen from the equation aforesaid, material removal rate is related to the pressure applied and the relative speed.

In CMP process, addition of slurry is needed, mainly because slurry would produce chemical reaction on wafer surface, making wafer material softened and thus increasing the material removal rate of CMP. As to discussion on weakening of interatomic bonding energy, most of the past studies used chemical reaction equation to interpret its physical phenomenon; but did not explore the quantitative numerical value of the produced change of bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at different temperatures.

The paper considers calculation of bonding energy of Morse potential energy of the single-crystal silicon dipped in slurry at different temperatures, and then explores and analyzes the relationship between the change of bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures and the cutting depth. First of all, the paper conducts an experiment of dipping single-crystal silicon in slurry at different temperatures, and calculates the SDFE value of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures and the thickness value of the chemical reaction layer. The paper also applies the innovative calculation method established by the paper to calculate the bonding energy value of Morse potential energy of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures, and then makes verification in order to understand the effects of different slurry temperatures on the bonding energy value of Morse potential energy of the chemical reaction layer of the single-crystal silicon. Finally, focusing on a fixed down force, and using SDFE theory and the SDFE value of the single-crystal silicon dipped in slurry at different temperatures, the paper calculates the cutting depth of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures, and explores how the change of bonding energy value of Morse potential energy of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures and the cutting depth are related to different temperatures of slurry for dipping. The slurry used is of volume concentration 50%; and the explored single-crystal silicon is dipped in slurry at the temperatures of 30ºC, 40ºC and 50ºC for 30 minutes respectively.

METHOD OF ADJUSTING DIFFERENT TEMPERATURES OF SLURRY FOR DIPPING OF SINGLE-CRYSTAL SILICON SUBSTRATE

In the aspect of control of dipping time, after single-crystal silicon substrate is dipped in slurry, the paper uses stopwatch as a tool to measure time and set the time of dipping for 30 minutes. In the aspect of control of dipping temperature, slurry is firstly poured into a beaker, which is then placed on the hot plate. Adjust the temperature knob on the heating device to different numerical values to achieve the slurry temperatures of 30ºC, 40ºC and 50ºC. In the heating process of slurry, thermometer is used to monitor the temperature. Once the slurry is heated to a specified temperature, use another beaker to hold the slurry, and dip the single-crystal silicon substrate in the heated slurry for 30 minutes.

During the dipping period of the single-crystal silicon substrate, slurry temperature decreases with the room temperature. Therefore, apart from using a thermometer to monitor the slurry temperature during the dipping period, if the slurry temperature starts to decrease, another beaker has to be used to hold the slurry on the hot plate, and the slurry is poured into the

beaker for dipping single-crystal silicon substrate. Meanwhile, a thermometer is used to monitor the slurry temperature. Through the way of heating slurry and the way of measurement by thermometer, it is ensured that during the 30 minutes' dipping time of the single-crystal silicon substrate in slurry, the temperature of slurry is controlled at ±1°C of the required temperature so as to achieve the experimental parameter of the temperature required.

THEORETICAL MODEL AND EXPERIMENTAL METHOD OF SDFE OF SINGLE-CRYSTAL SILICON DIPPED IN SLURRY AT DIFFERENT TEMPERATURES

The equipment of AFM used by the experiments of the paper is Dimension 3100 (D3100) AFM machine of Veeco Digital Instruments Inc. belonging to the nano-laboratory of Tungnan University. The cutting tool of probe used in the experiments is DT-NCHR diamond-coated carbon 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.

In the paper the SDFE value of single-crystal silicon dipped in slurry at a certain temperature is defined as the product obtained after multiplying the down force applied by the cutting tool of probe on the silicon substrate in the chemical reaction layer of slurry for silicon substrate dipped in slurry at a certain temperature, by the machining depth. It is just dividing the energy produced in the machining process by the volume removed from the silicon substrate by the cutting tool, and expressed as equation (1) as follows (Lin and Hsu 2012 ; Cook 1990):

$$\mathrm{SDFE}_{\mathrm{reaction}}(\text{specific down force energy}) = \frac{F_d \times \Delta d_1}{\Delta V_1} \quad (1)$$

where F_d denotes the down force that the cutting tool applies on workpiece; Δd_1 denotes the machining depth, and ΔV_1 denotes the workpiece volume removed by the cutting tool.

After down pressing and moving of the cutting tool, the depth in the middle area of the machined groove is gradually close to the fixed cutting depth. As to the removal volume after moving of the cutting tool, since machining is made in the above process, the volume at a distance of radius R behind the cap of the workpiece being cutted in by the probe in advancing direction has been removed.. Thus, during this time the removal volume is half of the spherical cap's volume under the cutting depth, and the removal volume is as follows:

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

where R denotes the radius of the probe tip of cutting tool; and d_1 denotes the cutting depth of the V-shaped groove at the first cutting pass on the first cutting layer.

It is supposed that the SDFE value of single-crystal silicon in the chemical reaction layer of silicon substrate dipped in slurry at a certain temperature in different axial directions during cutting of nanoscale V-shaped groove on single-crystal silicon is the same fixed value. Hence, the following equations in different axial directions can be obtained:

$$\mathrm{SDFE}_{\mathrm{reaction}} = \frac{\mathrm{F_z} \times \Delta \mathrm{dz}_1}{\Delta \mathrm{V}_1} = \frac{\mathrm{F_x} \times \Delta \mathrm{dx}_1}{\Delta \mathrm{V}_1} \quad (3)$$

Down force in Z axial direction:

$$\mathrm{F_z} = \frac{\mathrm{SDFE_{reaction}} \times \Delta \mathrm{V}_1}{\Delta \mathrm{dz}_1} \quad (4)$$

Cutting force in X axial direction:

$$\mathrm{F_x} = \frac{\mathrm{F_z} \times \Delta \mathrm{dz}_1}{\Delta \mathrm{dx}_1} = \frac{\mathrm{SDFE_{reaction}} \times \Delta \mathrm{V}_1}{\Delta \mathrm{dx}_1} \quad (5)$$

Here, $\Delta \mathrm{dz}_1$ denotes the cutting depth in Z axial direction; $\Delta \mathrm{dx}_1$ denotes the radius r_{cr} of spherical cap where the cutting tool for machining in X axial direction at the first cutting pass contacts with the workpiece; $\Delta \mathrm{V}_1$ denotes the cutting removal volume from workpiece at the 1st cutting pass; F_z denotes the down force; and F_x denotes the cutting force. Therefore, if the radius of the sphere of AFM probe tip has been measured, and if the $\Delta \mathrm{dz}_1$ of nanooscale V-shaped groove to be machined, as mentioned above, is known, during this time $\Delta \mathrm{dx}_1$ and $\Delta \mathrm{V}_1$ can be calculated according to the spherical size of the probe tip and the CAD software.

The paper substitutes the SDFE value of workpiece in the chemical reaction layer of slurry for dipping at a certain temperature, as obtained from experiments, in the SDFE equation (3) in different axial directions. Then equations (4) and (5) can be used to calculate the down force F_z and cutting force F_x of workpiece in the chemical reaction layer of slurry for dipping at a certain temperature when cutting nanoscale V-shaped groove on single-crystal silicon.

CALCULATION MODEL AND EXPERIMENTAL METHOD OF SDFE VALUE PRODUCED FROM CHEMICAL REACTION LAYER OF SINGLE-CRYSTAL SILICON SUBSTRATE DIPPED IN SLURRY AT DIFFERENT TEMPERATURES AND THICKNESS OF CHEMICAL REACTION LAYER

The paper considers the effects of the chemical reaction of the single-crystal silicon substrate dipped in slurry at different temperatures. As considered by the paper, the different temperatures of slurry for dipping of single-crystal silicon are 30°C, 40°C and 50°C, and the dipping time is 30 minutes. First of all, the paper conducts an AFM experiment, and calculates

the SDFE value of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at different temperatures as well as the thickness of the chemical reaction layer.

In the experiment of cutting single-crystal silicon substrate by AFM probe, the paper can obtain the $SDFE_{reaction}$ value of the chemical reaction layer on the single-crystal silicon surface affected by a certain slurry temperature, the $SDFE_{total}$ value of the chemical reaction layer exceeding the single-crystal silicon surface, and the $SDFE_0$ value of the single-crystal silicon of the slurry-free chemical reaction layer obtained from the experiment. In the AFM experiment, the paper sets a smaller down force F_z and measures Δd. Applying the $SDFE_{reaction}$ equation, the paper calculates the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at a certain temperature. Then the paper also employs a greater down force. Right now the cutting removal depth Δd_{total} of AFM probe would be greater than the thickness $\Delta d_{reaction}$ of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at a certain temperature, as shown in Figure 1.

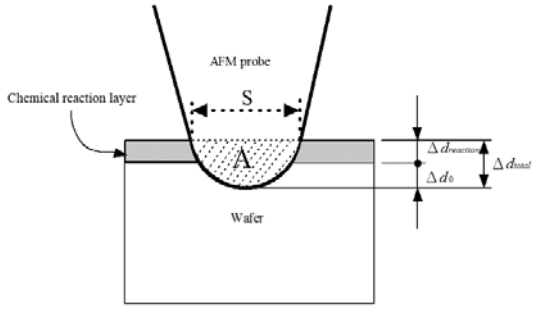

Figure 1 Schematic diagram of chemical reaction layer

Here, ΔV_0 denotes the removal volume of cutting depth Δd_0 beneath the chemical reaction layer of the single-crystal silicon substrate. The SDFE value of the single-crystal silicon substrate not being affected by chemical reaction is $SDFE_0$. If the diameter and down force F_{aw} of AFM probe are known, and can be seen from Figure 1, Δd_{total} can be known by measurement. Therefore, through equation (2), the removal volume ΔV_{total} can be achieved. And,

$$\Delta d_{total} = \Delta d_0 + \Delta d_{reaction} \quad (6)$$

Hence, the total down force energy is ($F_{aw} \times \Delta d_{total}$). And from the theoretic equation of SDFE, the following can be known:

$$F_{aw} \times \Delta d_{total} = SDFE_0 \times \Delta V_0 + SDFE_{reaction} \times \Delta V_{reaction} \quad (7)$$

The removal volume of thickness of the chemical reaction layer of single-crystal silicon substrate is

$\Delta V_{reaction}$, where $\Delta V_{reaction} = \Delta V_{total} - \Delta V_0$ (8)

Besides, from equation (7) and equation (8), the following equation can be derived:

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

And from equation (2), $\Delta V_1 = \frac{1}{2}\pi \Delta {d_1}^2 (R - \frac{\Delta d_1}{3})$, it is known that $\Delta V_0 = \Delta V_1$ and probe tip radius is R. Thus, $\Delta d_0 = \Delta d_1$ can be obtained.
Furthermore, this equation can be obtained:

$$\Delta d_{reaction} = \Delta d_{total} - \Delta d_0 \quad (10)$$

As mentioned above, since Δd_{total} can be acquired from measurement in experiment and Δd_0 can be obtained, equation (10) can be used to calculate the thickness, $\Delta d_{reaction}$, of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at a certain temperature.

CALCULATION METHOD OF BONDING ENERGY OF MORSE POTENTIAL ENERGY OF THE CHEMICAL REACTION LAYER OF SINGLE-CRYSTAL SILICON AFFECTED BY ITS BEING DIPPED IN SLURRY AT DIFFERENT TEMPERATURES

The lattice arrangement of the single-crystal silicon material explored in the paper is to add 4 atoms to FCC. The quasi-steady molecular statics nanocutting model of the paper takes Morse potential energy of two-body potential energy as a reference for calculating action forces between atoms (Tang 2007). Right now we have a great supposition in the quasi-steady molecular statics nanocutting simulation model that the parameters r_0 and α for Morse potential energy of the single-crystal silicon within the thickness of the chemical reaction layer for dipping single-crystal silicon substrate in slurry at different temperatures both remain unchanged, and only the bonding energy D value is changed. The main references are the parameters of interatomic balance distance (Å) r_0 and the material parameter ($Å^{-1}$)α, being a unit of size. The one with relation to the Si-Si bonding energy of the single-crystal silicon is the bonding energy D value

only.

According to the Morse potential used by the paper, a negative value of the gradient of Morse potential is taken to find the action force between two atoms, as expressed in equation (11):

$$F(r_{ij}) = -\frac{\partial \Phi(r_{ij})}{\partial(r_{ij})} = 2D\alpha\left\{e^{-2\alpha(r_{ij}-r_0)} - e^{-\alpha(r_{ij}-r_0)}\right\} \quad (11)$$

When $r > r_c$, the potential energy action tends to become zero. Thus, the cutoff radius is set to be r_c. When the distance exceeds r_c, since the action force of Morse force between two atoms has been very small, all of them will not be calculated.

When $r_{ij} = r_0$, the interatomic action force is exactly situated at a balance between attraction and repulsion. Thus, r_0 is set as the balance distance. The probe and workpiece are under the condition of no action force.

After action force is obtained, cutoff radius method is used. Increase a parameter δ for judging whether the distance of r_{ij} is greater than r_c . When the distance of r_{ij} is greater than r_c , there is almost no action of potential energy function. Hence, let δ be 0. On the contrary, when the distance of r_{ij} is smaller than r_c , action force will be produced. Then, let δ be 1. Subsequently, the interatomic action force can be calculated, which is shown in equation (12).

$$\vec{F}_i = \sum_{i=1}^{n} \vec{F}_{ij}\,\delta(r_{ij}) \quad \begin{array}{ll} if & r_{ij_c} \geq r_c \Rightarrow \delta = 0 \\ else & r_{ij} \leq r_c \Rightarrow \delta = 1 \end{array} \quad (12)$$

where *i* denotes the code of diamond probe atom; *j* denotes the code of workpiece atom in workpiece; *n* denotes the quantity of workpiece atoms; and r_{ij} denotes the distance between two atoms.

The numerical values of the produced action forces are the components of forces F_x, F_y and F_z of three axial directions, which are shown in equation (13):

$$\vec{F}_i = \vec{F}_{x_i} + \vec{F}_{y_i} + \vec{F}_{z_i} \quad (13)$$

where F_{x_i} denotes the force of component for action force in X direction; F_{y_i} denotes the force of component for action force in Y direction; and F_{z_i} denotes the force of component for action force in Z direction.

After cutting has been undergone for some time, there is not only one atom of workpiece affected by Morse force of diamond cutting tool. Therefore, the Morse force vector, affected by Morse force of diamond cutting tool at the new position of each workpiece atom after displacement in workpiece, is added to the Morse force of other workpiece atoms within cutoff radius at the new position of each workpiece atom after displacement, acquiring the sum of Morse force vector of each workpiece atom $\vec{F}_t$. 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 paper 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 paper as the cutting tool for cutting single-crystal silicon, the paper has to consider the correlation between C atoms of diamond probe and the atoms of single-crystal silicon workpiece. The numerical values of Morse potential parameters between atoms of Si-Si and Si-C used by the paper are shown in Table 1 (Tang 2007 ; Martin et al. 1986). The bonding energy D value (3.032ev) in Table 1 is the bonding energy value of Morse potential energy of the single-crystal silicon not being dipped in slurry.

Table 1. Parameter values of Morse potential energy of the single-crystal silicon, without being dipped in slurry, cut by the cutting tool of AFM diamond probe (Tang 2007 ; Martin et al. 1986)

	Si-Si	Si-C
D: bonding energy (ev)	3.032	0.435
α: material parameter ($Å^{-1}$)	0.7981	4.6487
r_0: interatomic balance distance (Å)	4.208	1.9475

The paper's innovative calculation method of bonding energy value of Morse potential energy of the chemical reaction layer of the single-crystal silicon affected by its being dipped in slurry at different temperatures is further explained below. The paper uses a fixed down-press depth for calculation. Such a fixed down-press depth is within the thickness of the chemical reaction layer of single-crystal silicon substrate affected by its being dipped in slurry at 30°C, 40°C and 50°C. Then the paper uses AFM experiment and SDFE theory to calculate the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon dipped in slurry at a certain temperature as well as the down force. After that, the bonding energy D value in Morse potential energy of the single-crystal silicon not being dipped in slurry is taken as an initially estimated

value. Such an initially estimated bonding energy value is $D_{initial}$. After $D_{initial}$ is substituted in molecular statics nanocutting model for simulation up to the same fixed down-press depth, the simulated initial down force can be calculated. The difference in down force F_d between two results calculated by the above two methods is taken as the objective function. The equation of the objective function is as follows:

$$\frac{|F_{dSDFES}-F_{dMS}|}{F_{dSDFES}} \leqq \varepsilon \quad (14)$$

Here, F_{dSDFEs} denotes the down force of the single-crystal silicon dipped in slurry at a certain temperature calculated by using SDFE method and the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at a certain temperature (30ºC, 40ºC and 50ºC); F_{dMS} denotes the down force calculated by molecular statics nanocutting model; and ε denotes the convergence value. According to the difference, the paper uses optimization method to step by step adjust the binding energy D value of Morse potential energy. When the two down forces converge to be a smaller ε value, 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 slurry at a certain temperature.

Finally, the paper uses the calculated bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate affected by its being dipped in slurry at a certain temperature. A probe with smaller radius size is adopted. Molecular statics nanocutting model is used to simulate the cutting force and down force for cutting of the single-crystal silicon affected by its being dipped in slurry at a certain temperature. The achieved results are compared with the cutting force and down force affected by the slurry temperatures of 30ºC, 40ºC and 50ºC calculated by using SDFE method and the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon dipped in slurry at a certain temperature, in order to prove that the bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate affected by the slurry temperatures of 30ºC, 40ºC and 50ºC is reasonable.

USE OF A FIXED DOWN FORCE TO ANALYZE THE RELATIONSHIP BETWEEN THE CHANGE OF BONDING ENERGY OF MORSE POTENTIAL ENERGY OF CHEMICAL REACTION LAYER OF SINGLE-CRYSTAL SILICON DIPPED IN SLURRY AT DIFFERENT TEMPERATURES AND THE CUTTING DEPTH

The smaller fixed down force set by the paper would make it not exceed the thickness of the chemical reaction layer of the single-crystal silicon dipped in slurry under the condition of different temperatures. Then the paper uses SDFE theory and the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures to calculate the cutting depth under a smaller fixed down force, and further analyzes how the calculated bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures is related to the acquired cutting depths and different temperatures of slurry for dipping. Besides, the paper compares the cutting depths obtained from simulation of the single-crystal silicon substrate not being dipped in slurry under the same fixed down force with the cutting depths of the single-crystal silicon substrate dipped in slurry at different temperatures and different temperatures of slurry for dipping. The paper also explores the difference in cutting depth in between.

RESULTS AND DISCUSSION

SDFE Value of Single-crystal Silicon not Being Dipped in Slurry

Under room temperature 23ºC and different down forces, the cutting depth result acquired from straight-line cutting experiment of the single-crystal silicon substrate without being dipped in slurry at the first pass is used to calculate by CAD software the volume removal amount of this depth. When SDFE concept is used for calculation, it is found that the $SDFE_0$ value of single-crystal silicon substrate without being dipped in slurry inclines to be a fixed constant:

$SDFE_0=0.01775(^{\mu N \cdot \mathrm{nm}}/_{nm^3})$。

$SDFE_{reaction}$ Value of The Chemical Reaction Layer of Single-Crystal Silicon Substrate Dipped in Slurry at Different Temperatures

Table 2 shows the AFM experimental results of different down forces in the chemical reaction layer of the single-crystal silicon substrate dipped in slurry with volume concentration of 50% and at the temperature of 30ºC for 30 minutes, and the $SDFE_{reaction}$ value acquired from calculation with the temperature of slurry for dipping at 30ºC. Using the results of the same experimental method, the average $SDFE_{reaction}$ values of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at the temperatures of 30ºC, 40ºC and 50ºC are obtained and shown respectively as follows:

$0.015943(^{\mu N \cdot \mathrm{nm}}/_{nm^3})$, $0.015528(^{\mu N \cdot \mathrm{nm}}/_{nm^3})$, and $0.014912(^{\mu N \cdot \mathrm{nm}}/_{nm^3})$.

Table 2. Down force, cutting depth, removal volume, and $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon substrate affected by slurry in the AFM experiment of the single-crystal silicon substrate dipped in slurry for 30 minutes (with slurry of volume concentration 50% at the temperature of 30°C)

Down force F(uN)	Cutting depth Δd_{z1}(nm)	removed volume $\Delta V_1(nm^3)$	$SDFE_{reaction}$ $(\mu N \cdot nm/nm^3)$
0.53	0.142	4.74953	0.015943
0.55	0.146	5.02083	0.015943
0.57	0.152	5.44191	0.015944
0.59	0.157	5.80576	0.015943
Average $SDFE_{reaction}$ value			0.015943

Calculation Results of The Thickness of The Chemical Reaction Layer of Single-Crystal Silicon Substrate Dipped in Slurry at Different Temperatures

The calculated thickness of the chemical reaction layer of the single-crystal silicon dipped in slurry at the temperature of 30°C is 0.2053nm. The calculated thickness of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at the temperature of 40°C is 0.2744nm. The calculated thickness of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at the temperature of 50°C is 0.3497nm. It can be seen that the larger thickness of the chemical reaction layer has with the silicon substrate dipped in slurry at higher temperature.

Calculation Result of Bonding Energy of Morse Potential Energy of Silicon Substrate Dipped in Slurry at Different Temperatures

The paper calculates the bonding energy D value of Morse potential energy of the single-crystal silicon substrate affected by its being dipped in slurry at different temperatures, and such calculation is carried out using a fixed down-press depth 0.14nm. Such a fixed down-press depth is within the range of thickness of the chemical reaction layer affected by slurry. Then the paper uses AFM experiment and SDFE theory to calculate the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures as well as the down force. After that, the bonding energy D_i=3.032ev of Morse potential energy of the single-crystal silicon not being dipped in slurry is taken as an initially estimated value. After D_i is substituted in molecular statics nanocutting model for simulation up to the same fixed down-press depth, the simulated initial down force can be calculated. The difference in down force F_d between two results calculated by the above two methods is taken as the objective function. The equation of the objective function is $\frac{|F_{dSDFES}-F_{dMS}|}{F_{dSDFES}} \leqq \varepsilon$.

Here, F_{dSDFES} denotes the down forces of the single-crystal silicon dipped in slurry at different temperatures calculated by using SDFE method and the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon dipped in slurry at the temperature of 30°C, 40°C and 50°C, and using probe radius R=2nm and down-press depth Δd=0.14nm, being 6.848 nN (30℃), 6.669 nN (40℃) and 6.405 nN (50℃) respectively; F_{dMS} denotes the down force of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures calculated by molecular statics nanocutting model; and ε denotes the convergence value.

The simulation parameters of three-dimensional molecular statics nanocutting model for calculation in the paper also includes R (probe radius) = 2nm and d (down-press depth) = 0.14nm. The probe goes down 0.0002nm in each simulation step. The distance between the place before the probe tip presses down and the material surface is 1 nm, implying that the probe contacts with the material at the 5,000th step. However, due to the effects of Morse potential energy, in the 3,300th step, just when the distance between the workpiece and the material is 0.34 nm, the distance between the probe atoms and the material atoms is closer, thus starting to produce repulsion. And in the 5,000th step, the probe starts to contact with the material. Right now the force is the down force produced from the contact between the probe and the material.

When single-crystal silicon substrate dipping in slurry at 30°C, D_0=3.032ev (bonding energy of Morse potential energy of Si-Si not being dipped in slurry) is firstly used for substituting in the equation of molecular statics nanocutting model, and $F_{dMS0} = F_{z0} = 7.779nN$ is calculated from the simulation, as shown in Figure 2.

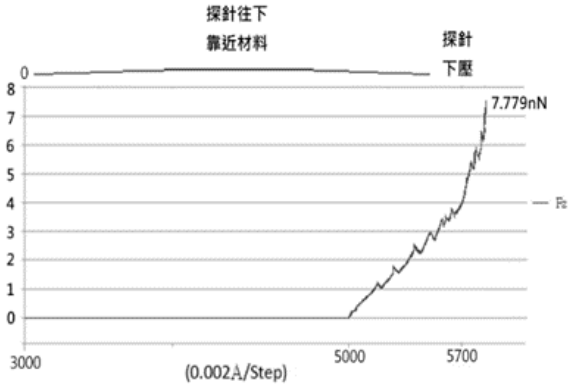

Fig. 2. Simulated down force of molecular statics nanocutting model with probe tip radius 2nm, down-press depth 0.14nm, and D value 3.032

After that, F_{dSDFES}(30°C)=6.848nN and $F_{dMS0} = 7.779nN$ are substituted in $\frac{|F_{dSDFES}-F_{dMS0}|}{F_{dSDFES}} \leqq \varepsilon_0$ for calculation, achieving $\varepsilon_0 \fallingdotseq 0.1359$.

The paper uses optimization method to step by step adjust the D value of Morse potential energy. The down force of a fixed down-press depth simulated by molecular statics nanocutting model is compared with the down force of a fixed down-press depth calculated by the $SDFE_{reaction}$ value of the single-crystal silicon affected by slurry at 30°C. After that, the step by step decreasing bonding energy D value is substituted in molecular statics nanocutting model for simulation, so as to prove whether ε value is decreasing continuously.

When the bonding energy D value is 2.719ev, the convergence value (ε) ≒ 0.00107. Comparing it with the convergence value (ε) ≒ 0.00116 when the bonding energy D value is 2.718ev, it is known that the bonding energy D value at this moment is adjusted to be less, and the convergence value ε has started to increase, and do not decrease anymore. In order to confirm whether the bonding energy D value of 2.719ev is an optimized value, the bonding energy D value of 2.717ev is substituted in the molecular statics nanocutting model for simulation of down press, and the acquired convergence value (ε) ≒ 0.00127. Comparing it with the convergence value (ε) ≒ 0.00107 when the bonding energy D value is 2.719ev, it is known that the bonding energy D value of 2.719ev is an optimized solution.

Finally, the bonding energy D value of 2.713ev is substituted in the molecular statics nanocutting model for simulation of down press in order to confirm whether the convergence value (ε) would increase continuously. The convergence value (ε) ≒0.00235 is obtained. It is greater than the convergence value (ε) ≒ 0.00107 when the bonding energy D value is 2.719ev. Therefore, it can be sure that when the bonding energy D value is smaller than 2.719ev, the convergence value starts to increase gradually. Finally, the above simulation results are rearranged. As drawn in Figure 3, X axis is the bonding energy D value, and Y axis is the convergence value (ε), showing the relationship between the bonding energy D value and the convergence value ε. Figure 4 shows the relationship between the partially magnified bonding energy D value of part A in Figure 3 and the convergence value ε. As seen from Figure 4, when D value is 2.719ev, there is a minimum convergence value ε. Therefore, 2.719ev can be taken as the bonding energy D value of Morse potential energy of the single-crystal silicon substrate dipped in slurry at 30°C.

Similarly, when single-crystal silicon substrate dipped in slurry at 40°C, the paper uses optimization method to step by step adjust the D value of Morse potential energy. The down force of a fixed down-press depth simulated by molecular statics nanocutting model is compared with the down force of a fixed down-press depth calculated by the $SDFE_{reaction}$ value

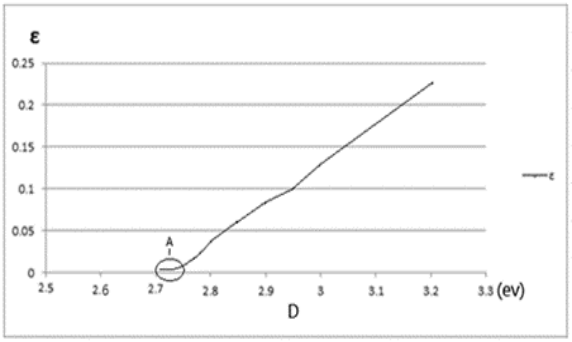

Fig. 3. Relationship diagram between the bonding energy D value of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at 30°C and the convergence value ε

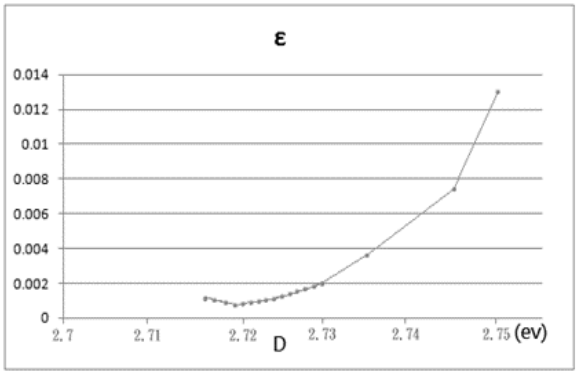

Fig. 4. Relationship diagram between the partially magnified bonding energy D value of part A in Fig. 3.and the convergence value ε

of the single-crystal silicon affected by slurry at 40°C. Finally, when the obtained D value is 2.648ev, there is a minimum convergence value ε. Therefore, 2.648ev can be taken as the bonding energy D value of Morse potential energy of the single-crystal silicon substrate dipped in slurry at 40°C.

Similarly, when single-crystal silicon substrate dipped in slurry at 50°C, and when the obtained D value is 2.543ev, there is a minimum convergence value ε. Therefore, 2.543ev can be taken as the bonding energy D value of Morse potential energy of the single-crystal silicon substrate dipped in slurry at 50°C.

As seen from the above calculation results, as the slurry for dipping has its temperatures of 30°C, 40°C and 50°C risen, the bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at temperatures of 30°C, 40°C and 50°C step by step decreases from 2.719ev (30°C), 2.648ev (40°C) and 2.543ev (50°C).

Verification of The Obtained Bonding Energy D Value of Morse Potential Energy of Chemical Reaction Layer of Single-Crystal Silicon Affected by Its Being Dipped In Slurry At Different Temperatures

As mentioned above, the different bonding energy D values of Morse potential energy of the single-crystal silicon substrate dipped in slurry at different temperatures are 2.719ev (30ºC), 2.648 ev (40ºC) and 2.543 ev (50ºC). Then the paper uses molecular statics nanocutting model to simulate cutting of a depth 0.14nm by a probe with tip radius 2nm. After simulation of the cutting force and down force for cutting of the single-crystal silicon dipped in slurry at different temperatures, a stable average down force and a stable average cutting force are taken, and the data obtained from the above simulation of molecular statics nanocutting model are rearranged in Table 3. Fig.5 shows stable average down force 6.853nN and stable average cutting force 1.305nN obtained from simulation of molecular statics nanocutting model with D value 2.719ev of the chemical reaction layer of the single-crystal silicon dipped in slurry at 30ºC and with probe tip radius 2nm and cutting depth 0.14nm.

Table 3. Stable average down force and stable average cutting force obtained from different bonding energy D values in the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at 30ºC, 40ºC and 50ºC after using three-dimensional molecular statics nanocutting model for simulation of cutting depth 0.14nm by probe tip radius 2nm

Simulation parameters		Stable average down force (F_z)nN	Stable average cutting force (F_x)nN
Bonding energy D value (ev)	Cutting depth (nm)		
2.719(30℃)	0.14nm	6.853	1.305
2.648(40℃)	0.14 nm	6.658	1.269
2.543(50℃)	0.14 nm	6.401	1.221

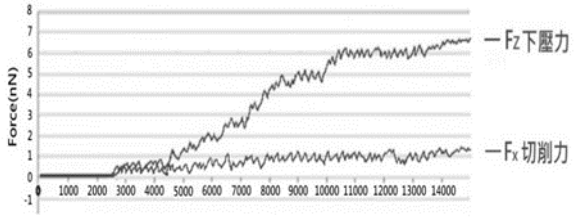

Fig. 5. Stable average down force 6.853nN and stable average cutting force 1.305nN obtained from simulation of molecular statics nanocutting model with D value 2.719ev of the chemical reaction layer of the single-crystal silicon dipped in slurry at 30ºC, and with probe tip radius 2nm and cutting depth 0.14nm

The stable average down force and the stable average cutting force obtained from simulation of the various bonding energy D values indicated in Table 3 are compared with the results obtained from calculation by SDFE method that the cutting force value 1.303nN and the down force value 6.844nN of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at 30ºC, the cutting force value 1.267nN and the down force value 6.651nN of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at 40ºC, and the cutting force value 1.219nN and the down force value 6.393nN of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at 50ºC. After comparing the cutting forces and the down forces among them, it can be proved that the difference among them is so small as around 1.44%. Therefore, the bonding energy values of Morse potential energy in the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at 30ºC, 40ºC and 50ºC are proved to be reasonable.

Use of A Fixed Down Force to Analyze The Relationship Between The Change of Bonding Energy of Morse Potential Energy of Chemical Reaction Layer of Single-Crystal Silicon Dipped In Slurry at Different Temperatures and The Cutting Depth

The paper uses a fixed down force to perform AFM experiment to cut the single-crystal silicon substrate not being dipped in slurry and those being dipped in slurry at different temperatures. The experimental method is that the single-crystal silicon substrate is dipped in slurry at different temperatures for 30 minutes. The various temperatures of slurry for dipping are 30ºC, 40ºC and 50ºC. Then the single-crystal silicon substrate not being dipped in slurry and those being dipped in slurry at different temperatures are used to conduct AFM cutting experiment. It is for setting of a smaller fixed down force 0.4μN. After that, AFM is used to carry out straight-line nanocutting and measurement of cutting depth, as shown in Table 4. The cutting depths are 0.098nm (not being dipped), 0.108nm (30ºC), 0.11nm (40ºC) and 0.114nm (50ºC).

Table 4. Cutting depths obtained from the single-crystal silicon substrate not being dipped in slurry at a fixed down force, and the cutting depth results of the single-crystal silicon substrate dipped in slurry at different temperatures (30ºC, 40ºC and 50ºC) in AFM experiment (with slurry of volume concentration 50% and dipping time of 30 minutes)

Temperature (ºC)	Down force F(μN)	Cutting depth d_z(nm)	$\Delta d_{reaction}$	Removal volume (nm^3)	$SDFE_{reaction}$
Not dipped	0.40	0.098	0.000	2.2624	0.017751
30	0.40	0.108	0.205	2.7476	0.015943
40	0.40	0.110	0.274	2.8503	0.015528
50	0.40	0.114	0.350	3.0613	0.014912

They are compared with the cutting depths calculated by SDFE method, being 0.096nm (not being dipped), 0.107nm (30ºC), 0.109nm (40ºC) and 0.114nm (50ºC). As seen from Table 4, the cutting

depth of the single-crystal silicon substrate not being dipped in slurry is smallest. And the higher the temperature of slurry for dipping, the greater the cutting depth of the chemical reaction layer of the single-crystal silicon substrate. Thus, it is proved that the difference between the cutting depth value of the single-crystal silicon substrate obtained by calculation method and the cutting depth value obtained by experiment is very small. Therefore, the result of cutting depth calculated by SDFE method is reasonable and acceptable.

Besides, from the previous results, it can be found that the slurry for dipping has its temperatures of 30°C, 40°C and 50°C risen, the bonding energy value of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate step by step decreases. Furthermore, when matching with the results in Table 4, the relationship between the change of bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate and te cutting depth can be known, as shown in Fig. 6. From Figure 6, it can be seen that with the continuous decrease of the bonding energy of Morse potential energy, the cutting depth would increase continuously.

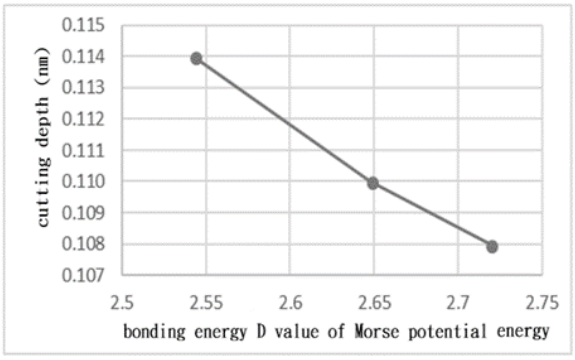

Fig. 6. Relationship diagram between the bonding energy D value of Morse potential energy and the cutting depth

CONCLUSION

The paper applies the theoretical model of bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate with chemical effect from slurry to calculate the bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at different temperatures (30°C, 40°C and 50°C). Then a very small down force is used to conduct AFM cutting experiment of the single-crystal silicon dipped in slurry at different temperatures. Using SDFE theory, the $SDFE_{reaction}$ value of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures can be acquired. The theoretical model for calculation of the thickness of the chemical reaction layer of slurry for dipping are employed to achieve the thickness of the chemical reaction layer of the single-crystal silicon dipped in slurry at different temperatures.

Under the circumstances of a fixed down-press depth and within the thickness of the chemical reaction layer, SDFE equation is used to induce the size of down force of the single-crystal silicon dipped in slurry at different temperatures. After that, in the process of using molecular statics nanocutting model to simulate dipping of the single-crystal silicon in slurry at different temperatures and at a down force of a fixed down-press depth, the paper calculates the bonding energy of Morse potential energy of the chemical reaction layer of the single-crystal silicon substrate dipped in slurry at different temperatures. Finally, the paper uses the calculated bonding energy D value of Morse potential energy of the single-crystal silicon affected by different slurry temperatures.

The cutting force and down force for simulated cutting of the single-crystal silicon dipped in slurry at different temperatures using molecular statics nanocutting model are compared with the cutting force and down force of the single-crystal silicon affected by different slurry temperatures obtained by calculation using SDFE method, in order to prove that the acquired bonding energy D value of Morse potential energy of the single-crystal silicon affected by different slurry temperatures is reasonable. In the final analysis the paper achieves the relationship between different slurry temperatures and the change of bonding energy of Morse potential energy. With the continuous rise of slurry temperatures of 30°C, 40°C and 50°C, the bonding energy of Morse potential energy decreases continuously. As to the relationship between the change of bonding energy of Morse potential energy and the cutting depth, with the continuous decrease of bonding energy of Morse potential energy, the cutting depth increases continuously.

ACKNOWLEDGEMENT

The authors would like to thank the support from Ministry of Science and Technology, Taiwan. (MOST 105-2221-E-011-045-MY3)

REFERENCES

Binning, G., Quate, C. F., and Gerber, C., “Atomic Force Microscope”, Physical Review Letters, Vol. 56, No. 9, pp. 930-933 (1986).

Cook, L. M., “Chemical Process in Glass Polishing”, Journal of Non-Crystalline Solids, Vol. 120, pp. 152-171 (1990).

Hu, S. Y., Ludwig, M., Kizler, P., and Schmauder, S., “Atomistic simulations of deformation and fracture of α-Fe”, *Modelling and Simulation in Materials Science and Engineering*, Vol. 6, No. 5,

pp. 567–586 (1998)

Irving, J. H. and Kirkwood, J. G., “The statistical mechanical theory of transport properties. IV. The equations of hydrodynamics”, *The Journal of Chemical Physics*, Vol. 19, Issue 9, pp. 817-829 (1950).

Jeng, Y. R., and Tan, C. M., “Study of Nanoindentation Using FEM Atomic Model”, *Journal of Tribology*, Vol. 126, Issue 4, pp. 767-774 (2004).

Lin, Z. C. and Hsu, Y. C., “A Calculating Method for the Fewest Cutting Passes on Sapphire Substrate at a Certain Depth Using Specific Down Force Energy with an AFM Probe”, Journal of Materials Processing Tech., Vol. 212, Issue 11, pp. 2321-2331 (2012).

Lin, Z. C., Jian, C. S. and Wang,R. Y., “A Study of Simulation of Three-Dimensional Quasi-Steady Molecular Statics Nanoscale Orthogonal Cutting of Single-Crystal Silicon Material Having Rows of Atoms with Vacancy Defect”, Journal of Chinese Society of Mechanical Engineering, Vol. 35, No. 4, pp. 257~265 (2014).

Lin, Z. C., Lin C. T. and Hsu Y. C., “Theoretical Model of Calculating Cutting. Force and Down Force for Nanocutting of V-Shaped Groove on Single-Crystal Silicon”, Journal of Chinese Society of Mechanical Engineering, Vol. 36, No. 5, pp. 363~374 (2015).

Martin, D. L., Thompson, D. L., and Raff, L. M. “Theoretical studies of termolecular thermal recombination of silicon atoms”, J. Chem. Phys., Vol. 84, No. 8. pp. 4426-4428 (1986).

Nanjo, H., Nony, L., Yoneya, M. and Aime, J. P., “Simulation of Section Curve by Phase Constant Dynamic Mode Atomic Force Microscopy in Non-contact Situation”, Applied Surface Science, Vol. 210, No. 1, pp. 49-53 (2003).

Preston, F. W., “The Theory and Design of Plate Glass Polishing Machines”, Journal of the Society of Glass Technology, Vol. 11, pp. 214-247 (1927).

Saraev, D., Kizler, P., and Schmauder, S., “The influence of Frenkel defects on the deformation and fracture of alpha-Fe single crystals”, *Modelling and Simulation in Materials Science and Engineering*, Vol. 7, No. 6, pp.1013–1023 (1999).

Tang, Q. H., “MD simulation of dislocation mobility during cutting with diamond tip on silicon”, Materials Science in Semiconductor Processing, Vol. 10, Issue 6, pp. 270-275 (2007).

Tseng, A. A., Jou, S., Notargiacomo, A., and Chen, T. P., “Recent Developments in Tip-Based Nanofabrication and its Roadmap”, Journal of Nanoscience& Nanotechnology, Vol. 8, No. 5, pp. 2167–2186 (2008).

受浸泡不同研磨液溫度影響之單晶矽莫氏勢能之結合能計算方法建立及分析

林榮慶 趙柏棠

國立台灣科技大學 機械工程系

摘要

本研究以比下壓能理論及計算化學反應層厚度理論模式的創新計算方法計算浸泡不同研磨液溫度之單晶矽莫氏勢能的結合能D值，再用分子靜力學奈米切削模式模擬切削單晶矽的切削力與下壓力，並進行驗證，以瞭解不同研磨液溫度對結合能的影響。最後針對固定下壓力，用比下壓能理論計算浸泡不同研磨液溫度單晶矽基板之切削深度，探討浸泡不同研磨液溫度之結合能的變化和切削深度的關係。