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Theoretical Model for Calculating the Thickness of the Nanoscale Chemical Reaction Layer on Sapphire Substrate for Different Slurry Dipping Durations and Experiments

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Keywords: Specific down force energy, atomic force microscopy, sapphire substrate, thickness of chemical reaction layer.

ABSTRACT

An innovative theoretical model and experimental method were proposed to calculate nanoscale thickness of the chemical reaction layer of sapphire substrates and analyze the various slurry dipping durations (dipping 5,10,20,30,60,90 min.)affecting the thickness of the chemical reaction layer. It involved applying small down force to cut sapphire substrates dipped in slurry for varying dipping durations it to obtain the SDFE values corresponding to the thickness of chemical reaction layer. The measured SDFE values of performing with a cutting depth interval of 0.05nm were then used to develop a theoretical method for calculating the thickness of the chemical reaction layer of sapphire substrate according to the various dipping durations of dipping slurry. Finally, an AFM nanoscale cutting experiment was conducted with a cutting depth interval of approximately 0.01 nm for each cutting pass to determine the changes in the SDFE values, which were used to measure the thickness of the chemical reaction layer for each slurry dipping time. The results verify that the proposed theoretical method is feasible. Next, it conducted a regression analysis and a regression equation for the thickness of the chemical reaction layer and various dipping durations. The results indicate that at longer slurry dipping duration, the chemical reaction layer thickened; specifically, the chemical reaction layer thickness at dipping duration less than 20 min increased rapidly with the dipping time, but at dipping duration longer than 30 min, the increase was approximately linear.

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INTRODUCTION

The chemical compositions in the slurry induce a chemical reaction with the material surface, generating chemical layer that are softer than the original material and easier to remove. Therefore, this study analyzed how varying the slurry dipping time for sapphire substrates influenced the thickness of the chemical reaction layer.

AFM is generally used for measuring and observing conductive and nonconductive surface patterns. Bining et al. (1986) was the first to implement atomic force microscopy (AFM) in 1986. AFM probes can be used as cutting tools and microstructures in semiconductors, optoelectronics, and metal surfaces (2008). Fang et al. (2000) used AFM probes in scribing experiments, and found that the scratch depth increased with the applied down force on the probe and the number of scribing cycle. The applied down force had the most notable effect. Yan et al. (2007) used an AFM diamond coated probe tip as a cutting tool to scratch Cu film deposited on a Si substrate. Tseng et al. (2010) used AFM probe tip to scratch Si wafer, determining that the depth and width of the scratched groove increased with both the applied down force and the number of scratching cycle. A regression analysis showed a logarithmic relationship between the dimension of the nanogroove and the down force of the probe, and a power-law function relationship between the dimension of the nanogroove and the number of scratching cycle. Currently, most studies on nanoscale cutting and scribing use Cu and Al as the cutting materials (2008)(2006). Peng et al. (2009) used AFM diamond probe to cut nanoscale groove in an Al film. Kanki et al. (2013) investigated the characteristics of chemical mechanical polishing CMP and utilized the chemical reaction layer formed by slurry to improve the planarization of the CMP. Various slurry pH values, dipping durations, and material electrolytic polarization characteristics were analyzed. Kanki et al. also sliced Cu specimens dipped in slurry, and the thickness of the chemical reaction layer was determined through transmission electron microscopy. Lin and Hsu (2012) used the concept of specific down force energy to propose a calculating method for the fewest cutting passes on sapphire substrate at a certain depth. However, the aforementioned studies have provided only approximate value or reference ranges regarding the thickness of the chemical reaction layer, and they did not calculate the thickness of chemical reaction layers accurately prior to CMP. Therefore, calculating or estimating the thickness of chemical reaction layers is critical. This paper developed an innovative theoretical model and experimental method based on the theory of specific down force energy (SDFE) to calculate the thickness of the chemical reaction layer of sapphire substrate for different slurry dipping durations. Simultaneously, a regression analysis was conducted to derive a regression equation for calculating the thickness of the chemical reaction layer of sapphire substrates after being dipped in slurry for various dipping durations.

EXPERIMENTAL APPARATUS AND METHOD PLANNING

Experimental Apparatus and Materials

Experiments were conducted using the Dimension 3100 atomic force microscope (Veeco, Digital Instruments) (2000) in the Nano Lab at Tungnan University, Taiwan. Sapphire substrates were used as the experimental material (diameter: 50.8mm (2 in).; thickness: 0.43 mm). Prior to nanocut the sapphire substrate, the section analysis function of AFM experiment was used to measure the surface topography and obtained that the smaller variation in the sapphire substrate surface was approximately 0.006 nm. AFM diamond coated probe was used to cut straight line groove into the sapphire substrate for observation. The sapphire substrate surface configuration was measured before and after cutting.

The AFM probe used in the experiment was a DT-NCHR diamond-coated probe. The thickness of the diamond coat was approximately 100 nm, and the semispherical tip of probe had a sphere radius of approximately 150 nm; thus, the diamond tip of probe was used as a semispherical cutting tool during the experiment. According to the manufacturer's instruction manual, the probe has a spring constant of 42 N/m and a resonance frequency of 320 kHz. To obtain a more accurate spring constant k_r, it used AFM in tapping mode to perform a frequency sweep to find the actual resonance frequency f_r of the probe. The natural frequency equation used in vibration mechanics, $f^2= k/m$, indicates that the square of the probe resonance frequency is proportional to the spring constant of the probe cantilever. Thus, the spring constant of the probe can be expressed as $k_r = (f_{r2} \times k_v) / f_{v2}$. The actual spring constant k_r of the experimental probe was calculated according to the resonance frequency f_v and spring constant k_v provided by the manufacturer and the measured actual resonance frequency fr (2012). Table 1 shows the resonance frequency and probe spring constant values used in the experiment.

Table 1 Resonance frequency and probe spring constant used in the experiment

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

In this study, the slurry was a colloidal silica suspension (pH 9.6, volume concentration: 50%; Allied High Tech Products, Inc.). This slurry is suitable to use in the CMP experiment of polishing sapphire substrate.

AFM Operation and Down Force Measurement of AFM probe

The AFM contact mode method was employed to accurately measure the down force applied during nanoscale cutting. First, the probe of AFM was pressed downward into the workpiece. The force–distance curve depicts the relationship between the setpoint and the offset of the probe cantilever. In the force calibration mode, the setpoint is the horizontal center of the force–distance curve. The setpoint can be set to obtain the cantilever offset d of the probe under down force. The down force F_d can be obtained using the following equation:

$$F_d = k_r d. \tag{1}$$

To determine the relationship between the setpoint and the down force of the AFM probe applied on sapphire substrate, prior to conducting the experiment, the different setpoints were set with the AFM contact mode. The cantilever offset d at each setpoint was substituted into Equation (1) to obtain the corresponding down force value.

Experimental Method Planning

Before nanocutting the sapphire substrate, the section analysis function was used with the AFM apparatus in contact mode to test the surface topography of the sapphire substrate. The smaller variance in the sapphire substrate's sectional surface topography was approximately 0.006 nm. Because this value is extremely low, relatively less down force than usual was applied for nanocutting in this experiment. This approach enabled accurately measuring the cutting depth of the sapphire substrate at different slurry dipping durations. Subsequently, the sapphire substrate was dipped in the slurry for 5, 10, 20, 30, 60, and 90 min to investigate the effect by the chemical reaction of the slurry on the thickness of the chemical reaction layer of the sapphire substrate.

For the experimental procedure, small down force was applied in cutting the sapphire substrates in order to find the baseline SDFE value of the sapphire substrate. Where the baseline SDFE value was the SDFE value without slurry dipping. Subsequently, small down force was applied in cutting sapphire substrates to determine the SDFE values corresponding to the thicknesses of the chemical reaction layer formed at different dipping durations of slurry. Next, a depth interval of approximately 0.05 nm and corresponding down force was applied to observe the SDFE value of the chemical reaction layer. When the SDFE value began to increase gradually after stabilizing, this indicated that the AFM probe had gradually penetrated the chemical reaction layer down to the original material which was not effect by the chemical reaction of the slurry. Therefore, the changes in SDFE value were critical targets. Then, the concept of SDFE was used to propose a theoretical method for calculating the thickness of the chemical reaction layer of sapphire substrates based on the effect of the chemical reaction of the slurry at various dipping durations. Finally, a nanoscale cutting at a depth interval of approximately 0.01 nm per cutting pass was conducted, and observed the data of changes in the SDFE value to measure the thickness of the chemical reaction layer at different dipping durations. Then, we verified the feasibility of the proposed method for calculating the thickness of chemical reaction layer of sapphire substrate.

REGRESSION ANALYSIS THEORY

Regression analysis is a statistical method for expressing the causal relationship between two or more measurement variables. The type of linear regression used for modeling in this study was the least squares method.

The generalized multiple linear regression model is defined as follows:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2^{\,2} + \cdots + \beta_P x^n_{\ p} + \varepsilon \quad (2)$$

where y is the thickness of the chemical reaction layer (i.e., the response variable) and x is the slurry dipping time in this study. Matrices were then used through the least squares method to determine the β coefficient. Thus,

$$Y = X\beta + \varepsilon \,. \quad (3)$$

If $Y = X\beta$ and $\varepsilon = 0$, then each side of the equation is multiplied by the

transposed matrix of matrix X to obtain $X'Y = X'X\beta$. Each side was then multiplied by the $(X'X)^{-1}$ matrix to obtain β. Therefore,

$$\beta = (X'X)^{-1} X'Y \quad (4)$$

The regression coefficient was shown as R^2, and R^2 was expected to approach 1 to make sure that the obtained regression equation was acceptable. R^2 can be shown as the following equation.

$$R^2 = 1 - \frac{SSE}{SST} \quad (5)$$

Where SSE is sum of squares of residual error. Usually, SSE was expected to approach zero. SST is sum of squares total.

Equations of SSE and SST are as follows.

$$SSE = \sum_{i=1}^{n}\left[Y_i - \hat{Y}(X_i)\right]^2 \quad (6)$$

$$SSE = \sum_{i=1}^{n}\left[Y_i - \hat{Y}(X_i)\right]^2 \quad (7)$$

Where Y_i is experimental value.

$\hat{Y}(x_i)$ is the calculated value from the regression equation.

$\overline{Y}$ is the average value of experimental results.

After establishing the regression model, we calculated the average residual values and regression coefficients to determine whether the regression model fit the experimental data. In general, smaller average residual values are more favorable, and the regression coefficient ideally converges to 1 to obtain a close fit and high explained variance. Such results confirm that a regression equation is highly reliable and representative of most experimental data (2012).

THEORETICAL MODEL FOR CALCULATION THE THICKNESS OF THE CHEMICAL REACTION LAYER

SDFE Theoretical Model and Calculation Method

The study considered that during the actual nanocutting process, down force is applied when the probe exerts sufficient downward force to achieve a certain depth in the workpiece for cutting in the cutting direction. The mechanism of the cutting process involves moving and removing particles at the atomic level. Thus, this is a model for estimating volume change. The specific down force energy, (SDFE), is defined below in equ. (8) (2012):

$$\text{SDFE} = \frac{F_d \times \Delta d_n}{\Delta V_n} \quad (8)$$

T where F_d is the down force exerted by the probe tool, Δd_n is the increase in cutting depth for cutting pass n, and ΔV_n is the volume removed from the workpiece for cutting pass n. Because the change in volume is relative to the increase in cutting depth, ΔV_n is a function of Δd_n.

In this study, we assumed that with the same workpiece material, the SDFE would be relatively constant, regardless of the down force and number of cutting passes. Additionally, because the probe tip was a semispherical cutting tool, the volume removed from the workpiece during the first cutting pass was determined using a geometric formula for spheres. Grooves were created in each cutting pass by pressing the semispherical cutting tool into the workpiece in a linear motion.

Observation of the groove configuration after the cutting experiment indicated that the probe tool initially penetrated the workpiece at a shallow depth; as the probe tool moved to an intermediate region, the cutting depth increased to a fixed value, thus increasing the removal volume. Therefore, to ensure that the cutting depth was in line with actual machining conditions, the average cutting depth was measured and calculated based on the intermediate region of the groove.

As mentioned, the volume of material removed on the first cutting pass was the volume of a spherical cap initially. At this point, the down-force removed volume is the volume of the spherical cap of the probe tip. The depth gradually became fixed after the tool was moved to the intermediate region of the cutted groove. Of the volume removed by the applied down force of the moving probe tip, the volume with a distance of radius R behind the spherical cap of the probe tip penetrating the workpiece in a forward direction was removed. At this time, the removed volume was half of the spherical cap volume and is expressed as follows:

$$V_1 = \frac{1}{2}\pi d_1{}^2(R - \frac{d_1}{3}) \quad (9)$$

where R is the probe tip radius of the cutting tool, and d_1 is the cutting depth during the first cutting pass. Besides, to stimulate and calculate removed volume, CATIA computer-aided design (CAD) software was also used to establish solid models of the geometric shape and cutting depth of the tool.

In the study, a fixed down force was applied to the workpiece. The radius of the probe tip and the cutting depth were used to calculate the workpiece volume removed during the first cutting pass. CAD software was used to simulate and calculate the workpiece volume removed following multiple cutting passes. The SDFE value was obtained by multiplying the down force with the cutting depth and dividing it by the removed volume, as expressed in Equation (8).

The SDFE value of Sapphire Substrate Not Dipped in Slurry

Table 2 shows the related AFM experimental data for the first cutting pass of the sapphire substrate without slurry dipping under various levels of down force and at room temperature (23 ºC). The results in Table 2 were input into the CAD software to calculate the volume removed at that depth. When SDFE equation was input into the calculation, it found that the SDFE values tended to approach the constant value of 0.1827 μN·nm/nm^3. Table 3 presents the AFM experimental results, it shows the cutting depths of the straight-line groove and SDFE values after multiple cutting passes on an sapphire substrate without dipping slurry onto which a down force of 35.93 μN was applied at room temperature. Table 3 shows that the mean SDFE value was approximately 0.1827 μN·nm/nm^3, which was assumed to be the baseline SDFE value (i.e. value of $SDFE_0$) in this study.

Table 2 AFM experimental data from the first cutting pass of straight-ling groove cutting of sapphire substrate without dipping in slurry at various levels of down force

downward force (μN)	measured cutting depth of the first cutting pass (nm)	Removed volume obtained by CAD calculation (nm³)	removed volume obtained by CAD calculation by theoretical equation(nm^3)	SDFE value obtained by CAD calculation ($\mu N\cdot nm/nm^3$)	SDFE value calculated by theoretical equation ($\mu N\cdot nm/nm^3$)
32.67	0.951	169.71	169.70	0.1829	0.1828
35.93	1.045	205.24	205.24	0.1828	0.1827
42.46	1.239	288.37	288.37	0.1824	0.1826
49.10	1.429	383.39	383.39	0.1830	0.1827

Table 3 AFM experimental data from the first cutting pass of straight-ling groove cutting of sapphire substrate without dipping in slurry at various levels of down force

downward force	cutting pass	measured cutting depth (nm)	removed volume obtained by CAD calculation (nm^3)	SDFE value ($\mu N\cdot nm/nm^3$)
35.93μN	1st	1.045	205.24	0.1829
	2nd	1.375	64.86	0.1828
	3rd	1.635	51.08	0.1829
	4th	1.860	44.27	0.1826
	5th	2.062	39.75	0.1826

The SDFE Value of Sapphire Substrate for Different Slurry Dipping Durations

In this study, sapphire substrate was the experimental specimen. The experimental parameters were the various dipping durations (5, 10, 20, 30, 60, and 90 min), the room temperature (23 ºC), and the volume concentration of the slurry (50%). In the following, it described more detail about how to obtain the SDFE values for the conditions that the sapphire substrate was dipped in slurry for 90 and 10 min. After dipping the sapphire substrate in slurry, applied a small down force for AFM nanoscale cutting of V-shaped groove to obtain the cutting depth and SDFE value of the chemical reaction layer of the slurry-dipped sapphire substrate. Initially, small down force was applied in the nanoscale cutting to ensure that the cutting depth would not exceed the thickness of the chemical reaction layer. Tables 4 and 5 show the results of dipping the sapphire substrate in slurry for 90 and 10 min, respectively. An AFM probe tip with radius of 150 nm was used for the experiment. A small down force was applied to cut the sapphire substrate to obtain the SDFE value of the chemical reaction layer, i.e., value of $SDFE_{reaction}$. The term Δd_z denotes the cutting depth and ΔV is the removed volume. Tables 4 and 5 show that when the sapphire substrate was dipped in slurry for 90 and 10 min, the average SDFE value of the chemical reaction layer (i.e., average value of $SDFE_{reaction}$) was 0.1622 $\mu N \cdot nm/nm^3$. Additionally, the tables indicate that the sapphire substrates attained identical SDFE values at 90 and 10 min of dipping time. Thus, when the room temperature and slurry volume concentration are constant, the dipping time exerts no influence on the SDFE value of the chemical reaction layer of the sapphire substrate. The same results were obtained when the sapphire substrates were dipped for 5, 20, 30, and 60 min.

Table 4 Down force, cutting depth, removed volume, and $SDFE_{reaction}$ value of the chemical reaction layer of AFM experiment on a sapphire substrate dipped in slurry for 90 min (slurry volume concentration: 50%; temperature: 23 ℃)

downward force F_d(μN)	cutting depth $\triangle d_z$(nm)	Removed volume $\triangle V(nm^3)$	$SDFE_{reaction}$ value ($\mu N \cdot nm / nm^3$)	Cutting width(nm)
2.10	0.055	0.7127	0.162212	8.094
2.15	0.056	0.7457	0.162212	8.117
2.26	0.059	0.8240	0.162208	8.512
4.26	0.111	2.9280	0.162207	10.722
4.30	0.113	2.9834	0.162203	10.781
4.36	0.114	3.0672	0.162204	11.154
Average $SDFE_{reaction}$ value			0.1622	

Table 5 Down force, cutting depth, removed volume, and $SDFE_{reaction}$ value of the chemical reaction layer of AFM experiment on a sapphire substrate dipped in slurry for 10 min (slurry volume concentration: 50%; temperature: 23 ℃)

downward force F_d(μN)	cutting depth $\triangle d_z$(nm)	Removed volume $\triangle V(nm^3)$	$SDFE_{reaction}$ value ($\mu N \cdot nm / nm^3$)	Cutting width(nm)
2.10	0.055	0.7127	0.162223	8.185
2.20	0.057	0.7729	0.162240	8.203
2.31	0.060	0.8566	0.162256	8.403
4.29	0.111	2.9337	0.162243	11.658
4.40	0.115	3.1153	0.162241	11.956
4.50	0.119	3.2993	0.162233	12.115
Average $SDFE_{reaction}$ value			0.1622	

The Effect of Slurry Dipping on Cutting Depth

According to the SDFE equation, cutting depth was 0.102 nm at the baseline SDFE value of 0.1827 $\mu N \cdot nm/nm^3$ and down force of 4.40 μN. Using an $SDFE_{reaction}$ value of the chemical reaction layer of 0.1622 $\mu N \cdot nm/nm^3$ and down force of 4.40 μN yielded a cutting depth of 0.115 nm as shown in Table 5. This result indicates that under a larger down force, a deeper cutting depth was obtained within the range of the thickness of the chemical reaction layer of sapphire substrate dipped in slurry.

Theoretical Model of Calculating the Thickness of the Chemical Reaction Layer

The proposed theoretical model for calculating the thickness of the chemical reaction layer of sapphire substrate dipped in slurry is an innovative model derived from SDFE theory. This method involves dipping the sapphire substrate in slurry for various dipping durations and performing AFM experiments to obtain the corresponding SDFE values for the chemical reaction layer. We combined this with the baseline SDFE value to calculate the thickness of the chemical reaction layer. The SDFE equation expresses the relationships between the SDFE value and the applied down force, cutting depth, and removed volume. After the substrates were dipped in slurry, the chemical reaction of the slurry with sapphire substrate generated a chemical reaction layer that had softer hardness than the hardness of the original material had. Therefore, SDFE theory was used to derive the theoretical model for calculating the thickness of the chemical reaction layer.

Figure 1 shows a schematic of the chemical reaction layer that formed on the sapphire substrate after it was dipped in slurry. In Figure 1, the assumption considered applying a large down force on the AFM probe to produce a straight-line cut on the sapphire substrate. Here, it assumed that the cutting depth Δd_{total} would be greater than the thickness of the chemical reaction layer $\Delta d_{reaction}$. If ΔV_0 denotes the removed volume of the removed depth Δd_0 below the chemical reaction layer in the sapphire substrate Δd_0 shows in Figure 1; $SDFE_0$ denotes the baseline SDFE value; R denotes the AFM probe tip radius; and F_d denotes the down force. And, if the values of $SDFE_0$, R and F_d had been known. Figure 1 indicates that Δd_{total} can be measured through the AFM experiment. Thus, equation (9) can be used to obtain the volume removed after the first cutting pass ,ΔV_{total}. Figure 1 also shows that

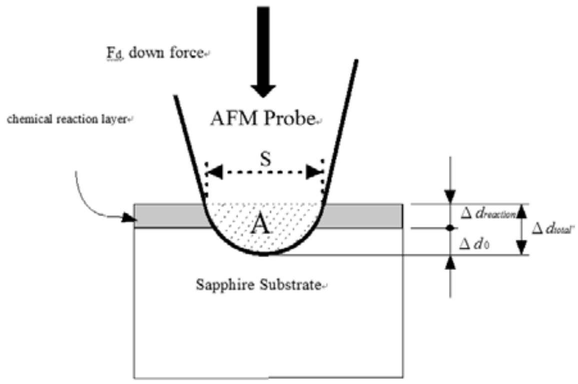


Fig. 1. Schematic diagram of chemical reaction layer

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

Therefore, the total down force energy is $F_d \times \Delta d_{total}$. Thus, based on equation(6) and SDFE theoretical equation, it can obtain that

$$F_d \times \Delta d_{total} = F_d \times (\Delta d_0 + \Delta d_{reaction}) = F_d \times \Delta d_0 + F_d \times \Delta d_{reaction}$$

$$= SDFE_0 \times \Delta V_0 + SDFE_{reaction} \times \Delta V_{reaction} \quad (11)$$

where ΔV_0 is the volume of the sapphire substrate removed by the AFM probe tip without the influence of the chemical reaction at depth Δd_0.

As mentioned, $SDFE_0$, ΔV_{total}, and $SDFE_{reaction}$ can be calculated and obtained from the measurement data by varying the down force and cutting depth applied in the AFM experiment for sapphire substrates without dipped slurry and the sapphire substrate dipped in slurry. The removed volume from the range of the thickness of the chemical reaction layer, $\Delta V_{reaction}$, can be calculated by equation (12) as follows:

$$\Delta V_{reaction} = \Delta V_{total} - \Delta V_0 \, . \qquad (12)$$

Thus, the following equation (13) can be deduced from (11) and (12)

$$\Delta V_0 = \frac{(F_d \times \Delta d_{total}) - (SDFE_{reaction} \times \Delta V_{total})}{SDFE_0 - SDFE_{reaction}} \qquad (13)$$

Additionally, equation (9) is $V_1 = \frac{1}{2}\pi {d_1}^2 (R - \frac{d_1}{3})$, the obtained ΔV_0 from equation(13) can be substituted for V_1 and because the tip radius R is known, therefore it can be obtain $\triangle d_0 = d_1$. Thus, it can deduced equation (14) from equation (10):

$$\Delta d_{reaction} = \Delta d_{total} - \Delta d_0 \qquad (14)$$

As above mentioned, when Δd_{total} is experimentally measured and Δd_0 can be obtained, equation (14) can be used to calculate $\Delta d_{reaction}$.

RESULTS AND VERTIFICATION

This study obtained experimental data at various dipping durations (5, 10, 20, 30, 60, and 90 min). Because identical SDFE values for various dipping durations and the same theoretical model were used in calculating the thickness of the chemical reaction layers, only the experiment involving a slurry dipping time of 90 min was used to demonstrate the analytical process of calculating the thickness of the chemical reaction layer. The calculation results of the thickness of the chemical reaction layer based on theoretical model with the various slurry dipping durations were then compared with these experimental results. Finally, we used the experimental data obtained at various dipping durations in the regression analysis and derived regression models for estimating and analyzing the thickness of the chemical reaction layer.

The SDFE Values at Different Cutting Depths for the Sapphire Substrate Dipped in Slurry

As mentioned, the SDFE value of the chemical reaction layer of the sapphire substrate dipped in slurry was 0.1622 μN·nm/nm^3. Subsequently, the experiments of cutting straight-line groove on the sapphire substrate through AFM were made with cutting depth controlled at an interval of approximately 0.05 nm. Figure 2 and Table 6 respectively show a part and all of the AFM results derived when various down force was applied on the sapphire substrates that were dipped in slurry for 90 min.

Additionally, Figure 3 depicts the experimental results shown in Table 6, which also lists the changes in the SDFE values. Because the previous experiment showed that the baseline SDFE value is 0.1827 μN·nm/nm^3, based on the changes in SDFE value (Table 6), it is reasonable to infer that when the SDFE values exceed that of the chemical reaction layer of the sapphire substrate dipped in slurry (i.e., 0.1622 μN·nm/nm^3), this indicates that the probe tip penetrated the chemical reaction layer to the sapphire substrate, which was unaffected by the slurry. Such penetration caused changes in the SDFE values. Therefore, it may be judged that the range of the thickness of the chemical reaction layer is related to the cutting depth that the SDFE value begins to change. This range can serve as a key reference indicator for calculating the thickness of chemical reaction layer. Additionally, Figure 3 depicts the relationships among the down force, cutting depth, and SDFE values derived from the sapphire substrate that was dipped for 90 min. The first half of the graph presented a flat line, indicating that the AFM probe tip was cutting in the range of the thickness of the chemical reaction layer. Therefore, this SDFE value is stable at 0.1622 μN·nm/nm^3. The sloped portion of the graph represents that the probe tip has penetrated the range of the thickness of the chemical reaction layer affected by the slurry. Hence, the SDFE value begins to increase as the down force and cutting depth increase. Finally, the line plateaued toward the later stage, implying that the cut has penetrated the entire the range of the thickness of the chemical reaction layer. Therefore, the SDFE value also approached the baseline SDFE value of sapphire substrate without dipping slurry, 0.1827 μN·nm/nm^3.

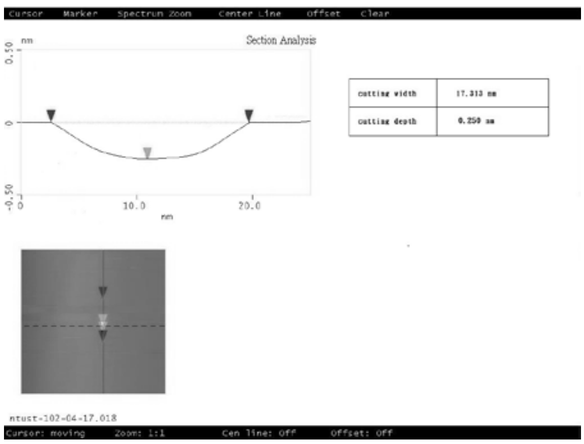
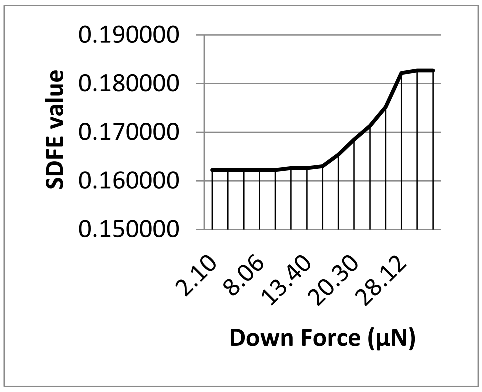


Fig. 2. Partial AFM experimental results under the following conditions: a cutting depth interval of approximately 0.05 nm, sapphire substrate dipped in 50% slurry for 90 min at 23ºC, down force of 9.55 μN, cutting depth of 0.250 nm, and cutting width of 17.313 nm

Table 6 Down force, cutting depth, removed volume, and $SDFE_{reaction}$ value from the AFM experiment (cutting depth interval: approximately 0.05 nm) on sapphire substrate dipped in 50% slurry for 90 min at 23℃)

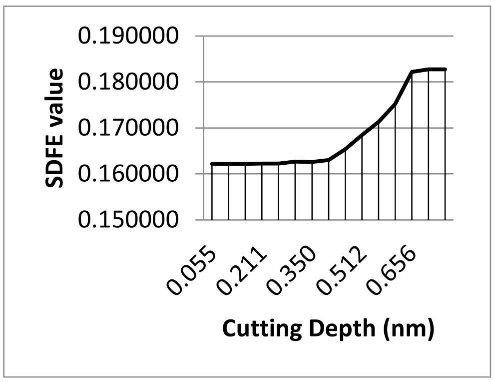
downward force F_d(μN)	cutting depth △ d_z(nm)	Removed volume △ V(nm^3)	$SDFE_{reaction}$ value ($\mu N \cdot nm / nm^3$)	Cutting width(nm)
2.10	0.055	0.7127	0.162223	8.185
2.20	0.057	0.7729	0.162240	8.203
2.31	0.060	0.8566	0.162256	8.403
4.29	0.111	2.9337	0.162243	11.658
4.40	0.115	3.1153	0.162241	11.956
4.50	0.119	3.2993	0.162233	12.115
2.10	0.055	0.7144	0.162212	8.094
4.17	0.109	2.7987	0.162212	10.304
5.69	0.149	5.2293	0.162214	13.368
8.06	0.211	10.4851	0.162238	15.907
9.55	0.250	14.7180	0.162233	17.313
11.92	0.311	22.8029	0.162650	19.339
13.40	0.350	28.8409	0.162616	20.482
15.62	0.407	38.9948	0.163030	22.058
17.52	0.450	47.6652	0.165404	23.220
20.30	0.512	61.6959	0.168465	24.766
22.70	0.563	74.5906	0.171337	25.968

(μN・nm/nm^3)



(a)

(μN・nm/nm^3)



(b)

Fig. 3. Relationship between (a) the down force and SDFE value and (b) the cutting depth and SDFE value derived from AFM experiment (cutting depth interval:approximately 0.05 nm) on a sapphire substrate dipped in 50% slurry for 90 min at 23 ºC

Calculation Result of the Thickness of the Chemical Reaction Layers after Different slurry Dipping durations

Table 6 shows the AFM experimental data at various down force values. The proposed theoretical model was applied to calculate the thickness of the chemical reaction layer of the sapphire substrate dipped in slurry for various durations. The results indicated the approximate thickness range of the chemical reaction layer affected by the slurry. Thus, the experimental values for the down force and cutting depth values where the SDFE values begin to change could be used to calculate the thickness of the chemical reaction layer. Through equations (13) and (14), the average thickness of the chemical reaction layer was calculated for a slurry dipping duration of 90 min. The results (Table 7) indicated that the average thickness of the chemical reaction layer of the sapphire substrate, $\Delta_{dreaction}$, was approximately 0.276 nm.

Table 7 Results of the proposed theoretical model for calculating the thickness of the chemical reaction layer for the sapphire substrate dipped in slurry for 90 min (average △dreaction: 0.2761nm) (slurry volume concentration: 50% ; temperature: 23 ℃)

Verification of the Theoretical Model Calculation Results

down force F_d (μN)	Δd_{total} (nm)	ΔV_{total} (nm^3)	$F_d \times \Delta d_{total}$	$SDFE_{reaction} \times \Delta V_{total}$	ΔV_0 (nm^3)	Δd_0 (nm)	$\Delta d_{reaction}$ (nm)
11.92	0.311	22.803	3.70888	3.698629	0.4995	0.035	0.2760
13.40	0.350	28.841	4.69000	4.677999	0.5854	0.0739	0.2761
15.62	0.407	38.995	6.35734	6.324961	1.5795	0.1308	0.2762
17.52	0.450	47.665	7.88400	7.731300	7.4488	0.1739	0.2761
20.30	0.512	61.696	10.39360	10.007083	18.8545	0.2357	0.2763
22.70	0.563	74.5906	12.78010	12.098599	33.2439	0.2868	0.2762
					average $\Delta d_{reaction}$: 0.276 nm		

The results of this study indicated that the proposed theoretical model is suitable for calculating the thickness of the chemical reaction layer of sapphire substrates dipped in slurry for various durations. To verify the feasibility of the proposed theoretical model, we also performed AFM experiments in which the primary consideration was the theoretical calculation result of the thickness of the chemical reaction layer. A cutting depth interval of approximately 0.01 nm and various down force values were used in the experiment. The experimental results were employed to verify whether the theoretical model provides reasonable results. Table 8 shows the SDFE values obtained from the experiments. The changes in SDFE can be used to determine whether the results from the theoretical model are consistent with those obtained experimentally. As demonstrated in Table 8, when the down force was 10.58 μN and the cutting depth was 0.277 nm, the SDFE value was 0.16227 μN·nm/nm3, which is similar to the SDFE value within the chemical reaction layer (i.e., 0.1622 μN·nm/nm3). When the down force was 10.89 μN and the cutting depth was 0.285 nm, the SDFE value was 0.162315 μN·nm/nm3, which is only slightly more than the SDFE value of 0.1622 μN·nm/nm3. This result indicated that the cutting depth exceeded the thickness of the chemical reaction layer. Thus, from the experimental results, we can infer that the sapphire substrate dipped in slurry for 90 min has a 0.277-nm thick chemical reaction layer. The calculations based on Table 7 yielded a thickness of 0.276 nm, which is extremely close; thus, the proposed theoretical model is feasible. In summary, the AFM experiment at a cutting depth interval of approximately 0.01 nm and the proposed experimental method for examining SDFE variations can be used to calculate the thickness of the chemical reaction layers of sapphire substrate dipped in slurry. In addition, the theoretical calculation model yielded reasonable results.

Table 9 shows the theoretical calculation and experimental results for the thickness of the chemical reaction layer of sapphire substrate at different slurry dipping durations. It demonstrates a slight difference between the theoretical calculation results and the experimental results , further verifying that the proposed theoretical model yielded reasonable results.

Table 8 The down force, cutting depth, removed volume, and SDFE value from the AFM experiment (cutting depth interval: approximately 0.01 nm) on the sapphire substrate dipped in slurry for 90 min (slurry volume concentration: 50%; temperature:23 ℃)

down force Fd (μN)	cutting depth Δdz (nm)	removed volume ΔV (nm^3)	values of SDFEz (μN·nm/nm^3)	cutting width (nm)
8.63	0.226	12.0285	0.162222	16.462
8.86	0.232	12.6754	0.162239	16.679
9.13	0.239	13.4517	0.162216	16.928
9.59	0.251	14.8360	0.162230	17.348
10.16	0.266	16.6616	0.162236	17.858
10.58	0.277	18.0604	0.162270	18.223
10.89	0.285	19.1159	0.162315	18.484
11.04	0.289	19.6465	0.162398	18.614
11.50	0.301	21.2930	0.162551	18.996

REGRESSION ANALYSIS OF EXPERIMENTAL RESULTS

A regression analysis was performed to clarify the relationship between the dipping duration and the thickness of the chemical reaction layer. A regression curve was plotted to predict the thickness of the chemical reaction layer at various slurry dipping durations. The fit between the regression curve and the experimental data was also verified. The regression analysis explored the effect of various slurry dipping durations on the thickness of the chemical reaction layer of sapphire substrate; the results were used to estimate the thickness of this layer at various dipping durations. To verify the fit between the regression curve and the experimental data, in the regression analysis, 15 min was added to the slurry durations in the experimental results. Subsequently, the reasonability of the regression curve was determined according to the regression coefficients and the residual values.

Table 9 Theoretical calculation results and experimental results for the thickness of the chemical reaction layer of sapphire substrate at different slurry dipping duration)

dipping time (min)	theoretical calculation results of the thickness of the chemical reaction layer (nm)	experiment-based thickness of the chemical reaction layer (nm)
90	0.276	0.277
60	0.264	0.264
30	0.251	0.253
20	0.246	0.245
10	0.222	0.221
5	0.101	0.101

Table 10 shows the experimental results for the thickness of the chemical reaction layer of sapphire substrates dipped in 50% slurry for 5 min, 10 min, 15 min, 20 min, 30 min, 60 min, and 90 min at a temperature of 23 ºC. These results showed that the thickness of the chemical reaction layer increased with the dipping duration, indicating that the duration effectively influenced the thickness of the chemical reaction layer.

Using the Table 10 results, we adopted the 30-min dipping duration as a demarcation point to derive two regression equations from the values of the thickness of the chemical reaction layer at different dipping durations. The regression equation for durations of 30, 60, and 90 min is a linear equation, whereas that for durations of 5, 10, 20, and 30 min is a cubic regression equation. Figure 4 shows the equations and regression curves. The dipping duration was denoted as x, and the obtained value for the thickness of the chemical reaction layer was denoted as y. To verify the experimental values for the cubic regression curve with dipping durations of 5, 10, 20, and 30 min, the experimental value for a dipping duration of 15 min was set as the reference value. The results in Figure 4 confirm that the cubic regression equation was reasonable for dipping durations between 5 and 30 min. Additionally, Figure 4 shows that the portion of the regression curve before the 30-min mark is relatively steep, indicating that shorter dipping durations greatly influenced the thickness of chemical reaction layer. The portion of the regression curve after the 30-min mark is relatively linear, indicating that at dipping durations more than 30 min, the changes in the thickness of the chemical reaction layer were smaller, approaching linearity. Table 11 shows the regression coefficients and average residual values of the various dipping durations, as well as the regression equation for estimating the thickness of the chemical reaction layer. The dipping duration is denoted as x, and the value of the thickness of the chemical reaction layer of the sapphire substrate is denoted as y. Table 11 shows that the regression coefficients for these two curves approach 1, and their average residual values are less than 0.03, indicating that these two regression equations are reasonably accurate.

Table 10 Thickness of the chemical reaction layer at various slurry dipping durations (slurry volume concentration: 50% ; temperature: 23℃)

dipping time (min)	thickness of the chemical reaction layer(nm)
0	0
5	0.101
10	0.226
15*	0.239*
20	0.246
30	0.251
60	0.264
90	0.276

*indicates the experimental parameters for verifying the regression curve.

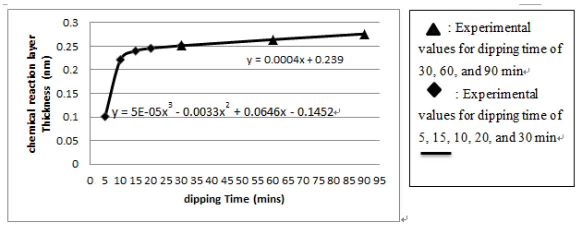


Fig. 4. Regression equation and curve for various dipping durations and chemical reaction layer thicknesses (slurry volume concentration: 50%; temperature: 23 ºC)

Table 11 Regression coefficients and average residual values of the regression model for dipping duration and the thickness of the chemical reaction layer

regression equation	y = 5E-05x3 - 0.0033x2 + 0.0646x - 0.1452
regression coefficient	0.9987
average residual value	0.028
regression equation	y = 0.0004x + 0.239
regression coefficient	0.9997
average residual value	0.025

CONCLUSION

In this study, SDFE theory was employed to establish a theoretical model for calculating the thickness of the chemical reaction layer of sapphire substrates for different dipping durations of slurry. In addition, AFM experiments with slurry dipping durations as the parameters were performed to verify the feasibility of the proposed model. First, the sapphire substrates were dipped in slurry for different durations. In the AFM experiments, a small down force was applied to obtain the SDFE values for the chemical reaction layer of sapphire substrate dipped in slurry. The sapphire within the chemical reaction layer was found to be softer than undipped sapphire. Subsequently, in the AFM experiments, various levels of down force and a cutting depth interval of approximately 0.05 nm were applied to obtain the SDFE values at various cutting depths. The SDFE value was found to increase with the cutting depth, and the thickness of the chemical reaction layer could also be determined from the changes in SDFE values. We then calculated the thickness of the chemical reaction layer by using the developed theoretical model .A cutting depth interval of approximately 0.01 nm was adopted to conduct AFM experiments. Using the AFM experiment results, we verified that the theoretical model produced reasonable results. A regression analysis was then performed using the experimental data obtained from the AFM experiments to establish the regression equations. The obtained regression curves exhibited a favorable fit with the experimental data and can thus be used to predict the thickness of the chemical reaction layer at various dipping durations. Furthermore, this study found that the SDFE value within the chemical reaction layer of sapphire substrate dipped in slurry was lower than the baseline SDFE value of undipped sapphire. Consequently, under the same down force, the cutting depth within the chemical reaction layer exceeded the cutting depth of the undipped sapphire substrate.

The results of this study also indicated that under fixed experimental conditions (i.e., fixed slurry temperature and volume concentration), the thickness of the chemical reaction layer increased with the dipping duration. Additionally, the experimental results and regression analysis indicated that when the sapphire substrate was dipped in slurry for up to 30 min, the chemical reaction layer thickened quickly. However, at dipping durations more than 30 min, we found that the change in the thickness of the chemical reaction layer was smaller and approximately linear.

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計算浸泡不同研磨液時間的藍寶石化學反應層厚度理論模式及實驗

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摘要

本文提出計算浸泡不同研磨液時間的藍寶石化學反應層厚度之理論模式和實驗方法。將浸泡不同研磨液時間的藍寶石用較小的下壓力切削藍寶石，以獲得浸泡不同研磨液時間的化學反應層內的比下壓能值(SDFE)。再用原子力顯微鏡(AFM)進行切削深度間隔 0.05nm 的藍寶石實驗，以獲得浸泡不同研磨液時間之不同切削深度的比下壓能值，用所得之 SDFE 值計算浸泡不同研磨液時間的化學反應層厚度理論模式，計算出浸泡不同研磨液時間的藍寶石化學反應層厚度值。最後再用 AFM 實驗切削藍寶石，其中的切削深度間隔為 0.01nm，並觀察其 SDFE 值的變化，決定浸泡不同研磨液時間的藍寶石化學反應層厚度的實驗值。最後驗證本文之計算浸泡不同研磨液時間的藍寶石化學反應層厚度理論模式為合理的。本文亦將所得之浸泡不同研磨液時間的藍寶石化學反應層厚度值進行迴歸分析，並獲得迴歸公式。迴歸分析結果可看出在浸泡時間小於 20 分鐘時，其化學反應層厚度增加很快，但在浸泡時間大大於 30 分鐘後，其化學反應層厚度的增加近似直線增加