How can we estimate the amount of C in CMP．
Ara Philipossian，University of Arizona
Ever since I starting working on copper CMP，I always wondered about the relative contributions of chemistry and mechanics to the process．Of course everyone knows that CMP takes advantage of the combined effects of chemistry and mechanics，but much to my surprise，the answer to my question was not published anywhere（at least to my knowledge）and the available information was mostly anecdotal．In fact，for about 6 months，at conferences or meetings，I would pose this question to ex－colleagues and industry experts and the answers which I would get seemed to indicate that chemistry accounted for roughly 60 to 80 percent of the overall copper polish process．

I started thinking about this question in greater depth，but could not really come up with an experimental plan to shed light on the subject．One day，one of my Ph．D．students，Jam Sorooshian，came to me with some copper removal rate results he had obtained by varying platen temperature，wafer pressure and relative pad－wafer velocity using consumables donated to us by our friends at Fujimi（PL－7102）and Rodel－Nitta（IC－1000）．

His results were in the form of isotherms on a removal rate versus $P^{\prime} U$ graph． We started discussing the results together and suddenly I noticed that the $y$－intercept of the isotherms，which in theory represented the dynamic etch rate of copper，was higher at elevated platen temperatures．I immediately realized that we had accidentally hit the jackpot，and that，given some time，we could determine the relative contribution of chemistry in copper CMP after all ！

It was 6 PM．That evening，after the pizza delivery guy left my office，Jam and I quickly began to develop a simple model based on the Arrhenius rate expression and the generalized Preston＇s model．

In Preston＇s equation below，

$$
\mathrm{R}=\mathrm{k} \cdot \mathrm{Pn} \cdot \mathrm{U}^{\mathrm{m}}+\mathrm{RR}_{0}
$$

$R R$ is the material removal rate，$k$ is the Preston＇s constant，$P$ is the applied wafer pressure，$U$ is the average linear pad－wafer velocity，and RRo represents the dynamic etch rate of the material in the absence of pressure and velocity． This equation is very general since it relies on essentially one constant，$k$ ，to account for all chemical and mechanical intricacies of the process．It was obvious that this needed some work！

Jam quickly began working on a new definition of Preston＇s constant，$k$ ，which considers the effect of polishing temperatures through an Arrhenius relationship and a newly defined＇thermally independent constant＇，kappa．In the equation below，E denotes the overall activation energy of the process．Jam＇s newly defined activation energy describes all events，chemical or mechanical，that were impacted by temperature during CMP． R and T represent the gas constant and the temperature of the process，respectively．

$$
\mathrm{k}=\kappa \exp \left(\frac{-E}{R T}\right)
$$

Incorporation of the above definition into Preston＇s equation can be further manipulated to generate a linear relationship between removal rate and the inverse of temperature．In this study，effective removal rate is defined as the component of the total removal rate at non－zero wafer pressures and pad－wafer velocities in accordance as follows：

$$
R R e=R R-R R o
$$

Through a logarithmic rearrangement，Preston＇s equation becomes：

$$
\ln (R R e)=\frac{-E_{\text {chemical }}}{R T} \ln (\kappa)+\ln \left(P^{n \cdot} \cdot U^{m}\right)
$$

By plotting the natural log of the effective removal rate versus the inverse of temperature，an Arrhenius relationship for the process could easily be described with $E$ representing the overall activation energy of the process．Based on our data，the overall activation energy for the set of consumables used by Jam was roughly 50 kJ per mole．

I then proceeded to apply the above equation one more time to the dynamic etch rate data（which by definition did not include any mechanical phenomena）to obtain the true chemical activation energy of the process：

$$
\ln (R R e)=\frac{-E_{\text {chemical }}}{R T} \ln (\kappa)
$$

Our data indicated that the true chemical activation energy of the process，based on the dynamic copper etch rate，would be approximately 34 KJ per mole．

It was past 9 PM．Based on our simple analysis，the ratio of these two activation energies would then represent the relative contribution of chemical phenomena to copper CMP，which was calculated to be roughly 70 percent for the PL－7102 and IC－000 consumables set．

I believe that the above methodology can be used to analyze additional consumables sets such as Hitachi Chemical＇s abrasive－free slurry or Cabot＇s alumina－based slurry in conjunction with Rodel＇s IC－1000 and JSR WSP pads．Of course，in these cases，we expect results to be different altogether since each specific consumables set will have its unique set of activation energies．We plan to start these new tests on April after Spring Break．I hope to have the honor of presenting this data some day to the JSPE in Tokyo．Until then，I maintain that 70 percent（which is within the anecdotal range of $60 \sim 80$ percent figure）is a good enough number since at least we have some theory to back up our results．

I hope I have not bored the readers with too many equations．I tried getting rid of the equations，but quite honestly，there was no other way to get the message across without some theoretical analysis．Your comments and suggestions regarding the contents of this article will be much appreciated．By the way，I just passed Mount Fuji on the left．What a magnificent sight！

March 18， 2003
Seat 11A，Green Car No． 9 on Nozomi 44 en route from Nagoya to Tokyo．


No．1：With students and friends at my house in Arizona No． 1 ：アリゾナの自宅での学生と友人達


No．2：Taking visitors on a tour of the UA campus No．2：アリゾナ大学のキャンパスでゲストを案内


No．3：Giving a presentation at the recent CMP－MIC Conference in Marina Del Rey， California
No．3：カリフォルニア州マリナデルレイで開催された最近のCMP－MIC会議でのプレゼンテーション


No．4：Spending some time off from work with my students No．4：研究室の学生たちとの休憩

