Etch Rate Studies of Base Catalyzed Hydrolysis of Polyimide Film. II

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SYNOPSIS

The influence of a potassium carbonate (K_2CO_3) additive on the base catalyzed hydrolysis of polyimide (Kapton†) film in aqueous potassium hydroxide (KOH) was determined experimentally. The etch rate is significantly greater for KOH/K_2CO_3 solutions compared with solutions composed of KOH only. The experimental order of the reaction with respect to the KOH concentration was found to be 1.5. In addition, the rate was found to increase linearly with respect to the K_2CO_3 concentration at a fixed KOH concentration. Visual observations of a thinner gel layer on the surface of the film, combined with increased solubility of the etch by-products in KOH/K_2CO_3 relative to KOH, help to explain the difference in etch rate. It appears the ability of K_2CO_3 to enhance the solubility of the hydrolyzed polyimide (polyamic acid salt) results in faster etch rates.

INTRODUCTION

Polyimide film is used extensively as a dielectric insulating layer in flex circuitry and microelectronics applications because of its good chemical, mechanical, and electrical properties.[1-3] In particular, Kapton polyimide film is the workhorse of the electronics industry. Kapton is prepared via the polycondensation of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) in *N,N*-dimethylacetamide (DMAc), forming the corresponding polyamic acid. The polymer solution is chemically imidized using the appropriate chemicals, followed by a heat treatment to remove solvent and conversion chemicals and to also complete the imidization.[4] Kapton HN contains a slip additive, phosphate of calcium, but Kapton H does not.[5]

Patterning the dielectric is an important step in microelectronics processing as it can provide increased design and product flexibility. These patterns may be formed by mechanical means or chemically using plasmas or wet etchants. Polyimide can be etched using aqueous base at elevated temperatures.[6-8] The effect of alcohol type and concentration on etch rate, when alcohol/water/KOH solutions are used to etch Kapton, have been described by Kreuz and Hawkins.[9,10] An increase in the etch rate was found for solutions containing about 80 wt % alcohol and 20 wt % water compared with pure water systems at similar KOH concentrations. Although isopropanol and *n*-propanol were found to increase the etch rates above that of ethanol at 0.1*M* KOH, the ability of ethanol/water mixtures to dissolve higher KOH concentrations (e.g., 1.0*M*) results in higher overall etch rates. One proposed explanation was plasticization of the Kapton by the alcohol, allowing faster penetration of the hydroxide anion into the film.[9,10] Subsequent work by Stern[11] showed that the rate of alcohol permeation through Kapton is orders of magnitude lower than that of water, indicating the concentration of alcohol in the Kapton would be too low to plasticize the film. Another postulation is that the attacking hydroxide anion is less solvated at high alcohol concentrations and thus reacts with the polyimide more readily.[9,10]

The kinetics of the base catalyzed hydrolysis of Kapton H over a range of temperatures and concentrations of aqueous potassium hydroxide (KOH) was reported in an earlier publication.[12] It was dem-

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† Kapton is a registered trademark of E.I. DuPont de Nemours & Co.

Journal of Applied Polymer Science, Vol. 43, 1379–1383 (1991)
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onstrated that the experimental etch rate was second order with respect to KOH concentration over the range tested. In addition, a faster etch rate was observed in the first 5-sec etching compared with a steady-state etch rate found during 30-sec etch intervals. It was proposed that formation of a gel layer at steady state was an important factor in regulating the dissolution of partially reacted polyamic acid salts from the surface of the film during etch. Kreuz and Hawkins[9] reported the presence of a gel layer on the surface of the film at 77% ethanol solution as well. In this article, the effect of K_2CO_3 on the etch kinetics of Kapton films in KOH/K_2CO_3 solutions is reported. Additional insight is provided regarding the influence of K_2CO_3 on the etching mechanism.

EXPERIMENTAL

Kapton H film (2 mils thick) was cut into 0.75 × 1.25″ samples and a hole punched in the middle using a single-hole punch. The samples were stored at ambient until use. Aqueous KOH and KOH/K_2CO_3 solutions were prepared by mixing a known quantity of KOH (Fisher, ACS grade, approximately 15% water) and K_2CO_3 (Aldrich, 98%) with deionized water to a predetermined volume. The Kapton samples (four per condition) were weighed using an analytical balance. The samples were placed in a 95°C deionized water presoak bath for 2.5 min, in the KOH or KOH/K_2CO_3 etching solution for the specified time at 95°C, rinsed in a separate hot deionized water bath at 95°C for 2.5 min, and finally in a room temperature deionized water rinse for 15 min. Samples were then stored at ambient for 24 h prior to reweighing.

Etch rate measurements were made as a function of KOH concentration (1–7*M*) at a fixed K_2CO_3 concentration of 2.2*M* (Fig. 1). In all cases, the concentrations were not corrected for activities. The reaction orders discussed herein are experimental orders only (i.e., they do not represent the order of elementary reactions). In addition, the etch rate, relative to the K_2CO_3 concentration (at fixed KOH concentrations of 6.7 and 2.7*M*), was determined. The K_2CO_3 concentration was varied from 0.5–4*M*. The activation energy was found using a solution composed of 6.7*M* KOH and 2.4*M* K_2CO_3 at 70, 75, 80, 85, 90, and 95°C. Average rate measurements

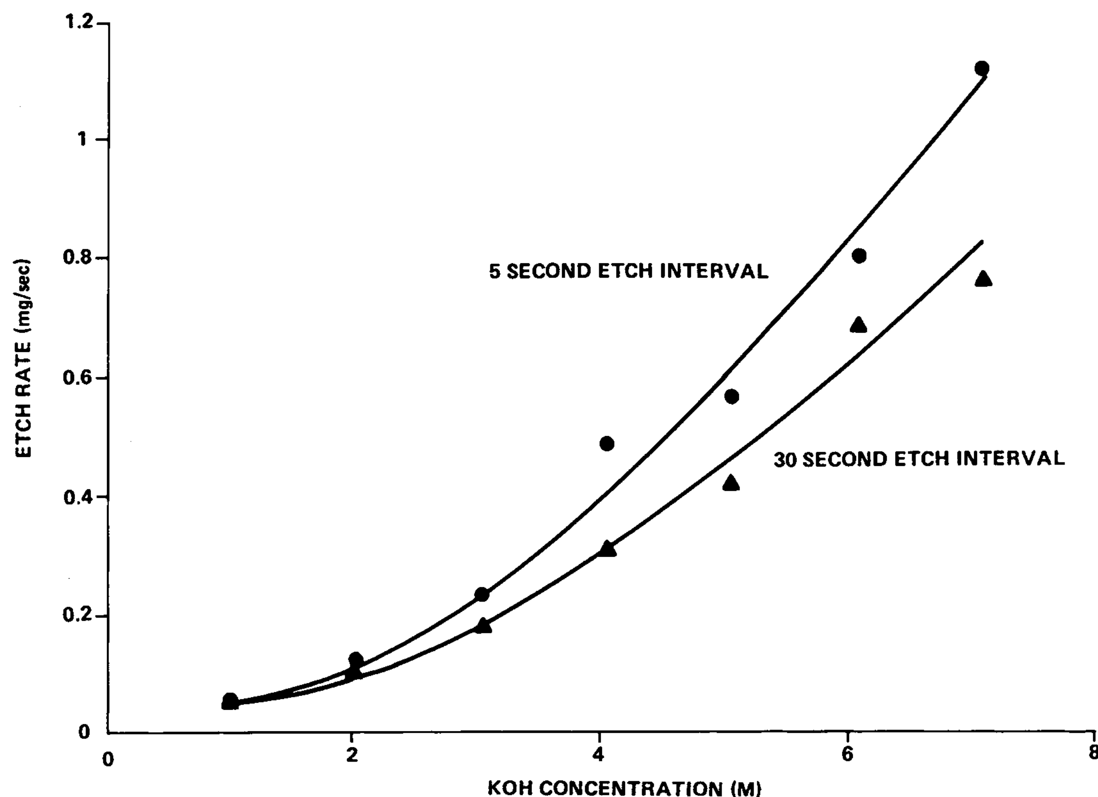

Figure 1 Etch rate as a function of KOH concentration. K_2CO_3 concentration was maintained at 2.2*M*.

were calculated by dividing the weight of material etched by the exposure time in the etch bath (all rates are reported as mg/sec). Five and 30-sec immersion times in the etch bath were used to determine all etch rates. Previous work with KOH solutions[12] indicates there is a higher etch rate in the first 5 sec etching relative to steady state. Steady-state etch rates are achieved after 5–10 sec. Therefore, 30 sec was selected as a reasonable etch time to achieve steady-state etch rates.

A gel layer is observed on the surface of the Kapton after removal from the KOH solution; however, a significant decrease in the thickness of this gel layer is observed for samples etched in KOH/K_2CO_3. Kreuz and Hawkins[9,10] observed a swollen, solvated gel on the film surface when etching Kapton in ethanol/water/KOH solutions at low KOH concentrations.

A comparison of the etch rate vs. K_2CO_3 concentration shows that the etch rate varies linearly with the K_2CO_3 concentration in the data range investigated (0.5–4M), as is shown in Figure 2. At K_2CO_3 concentrations greater than 4M, the additional K_2CO_3 was difficult to dissolve. The KOH concentration for this experiment was maintained at a constant concentration of 2.7M. A linear fit provides a higher correlation coefficient than does a power fit for this data. Similar data have been collected at a fixed KOH concentration of 6.7M (Fig. 3). In this experiment, an etch rate maximum at approximately 2M K_2CO_3 is found. The maximum is caused by solubility limitations in the supersaturated etch solution at higher K_2CO_3 concentrations. Comparing the rate data collected at 6.7M for a KOH solution only with a solution containing 6.7M KOH/1.9M K_2CO_3 indicates that the K_2CO_3 enhances the etch rate by 40–50% relative to the rate achieved with KOH alone. Certainly, the K_2CO_3 significantly enhances the overall dissolution mechanism.

The activation energy for the etch reaction was determined for both 5- and 30-sec etch intervals using a 6.7M KOH/2.4M K_2CO_3 solution. Calculated activation energies are shown in Table I for KOH solutions with and without K_2CO_3. The solutions show a similar activation energy for both the 5- and 30-sec etch intervals although the activation energies for the KOH/K_2CO_3 solution are slightly lower. This trend is consistent with the earlier rate data,

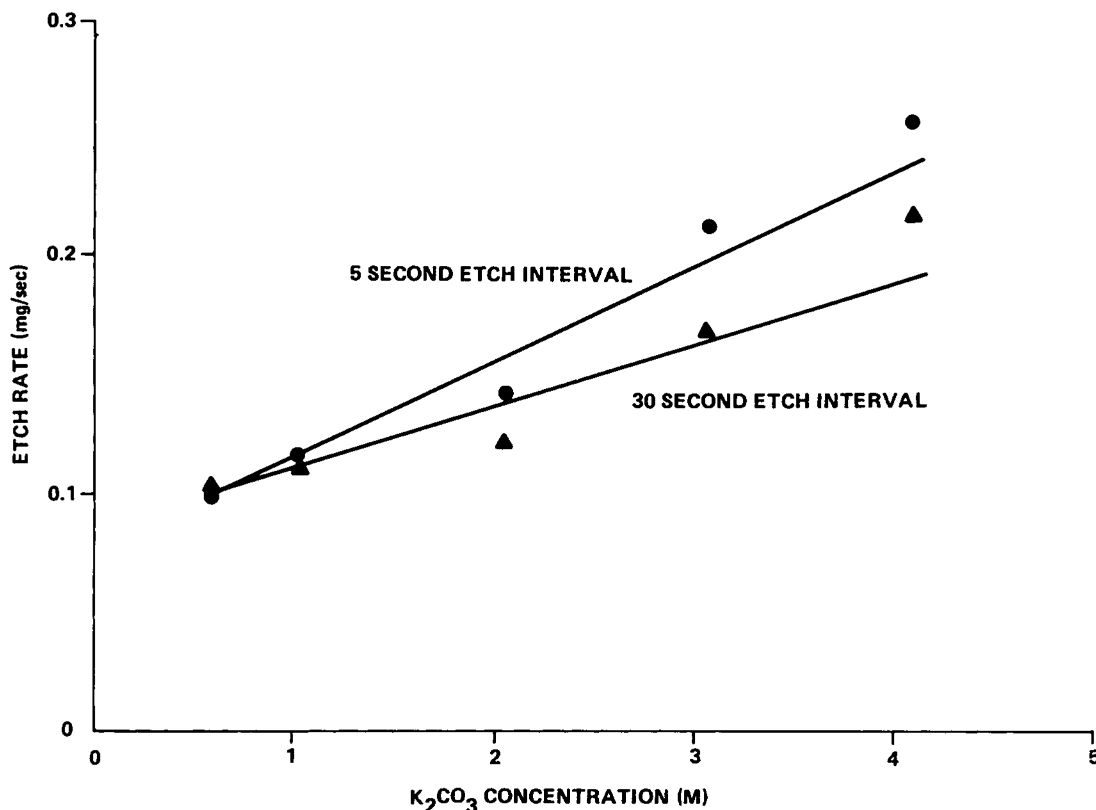

Figure 2 Etch rate vs. K_2CO_3 concentration. KOH concentration was maintained at 2.7M.

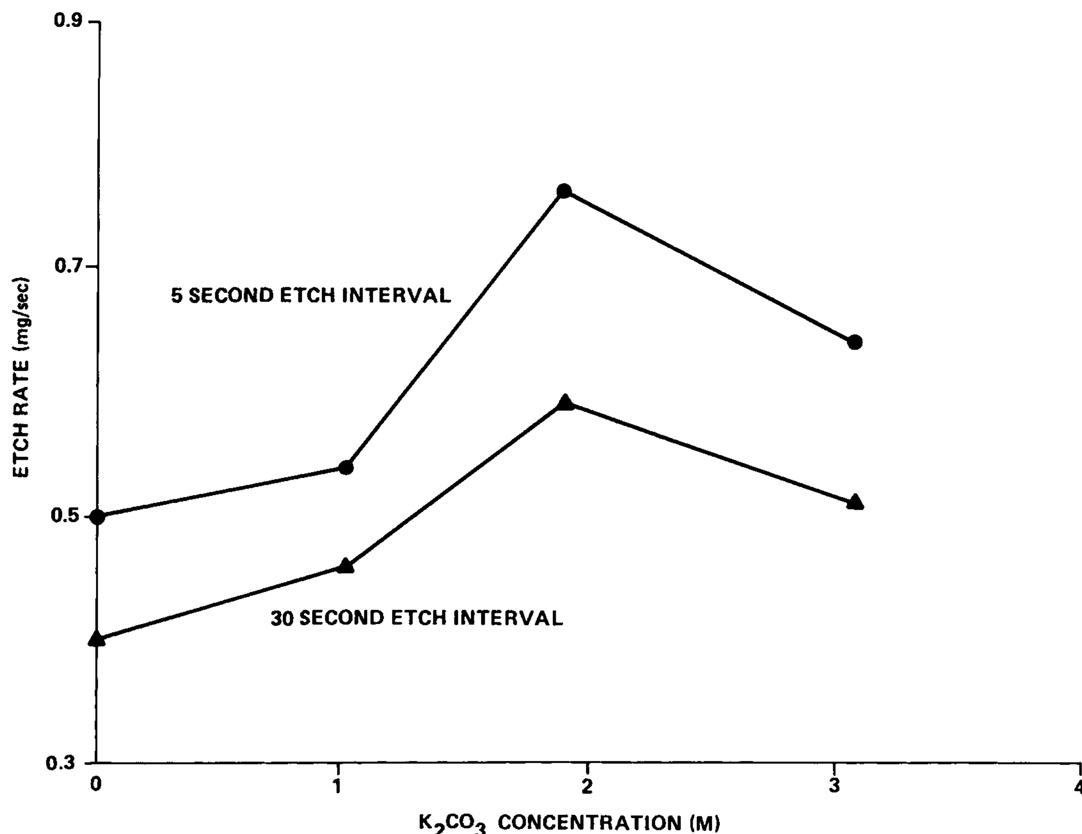

Figure 3 Etch rate as a function of K_2CO_3 concentration. KOH was maintained at 6.7*M*.

indicating a higher etch rate for the KOH/K_2CO_3 solution vs. the KOH-only solution.

As indicated in the previous work,[12] the etch mechanism entails base catalyzed hydrolysis of polyimide at the imide ring to form the corresponding polyamic acid salt. Whether cleavage occurs at various defect sites or complete conversion of the polyimide to the salt occurs is not clear. Rutherford backscattering (RBS) analysis by Matienzo and Emmi[13] indicates K+ is mostly at the surface of Kapton etched with KOH and does not diffuse into the bulk. Thus, the etch mechanism is likely inhibited by the dissolution process at the surface of KOH-etched samples. The reduction in the gel layer observed on KOH/K_2CO_3-etched Kapton, along with the accompanying increase in overall relative average etch rate, indicates that K_2CO_3 enhances this overall mechanism by improving the total dissolution of the etch products. A noticeable decrease is observed in flocculant (etch by-products) in the bath when using KOH/K_2CO_3 as the etchant, suggesting the etch by-products are more soluble in this solution as well. However, as with solutions of KOH only, the rate measurements consisting of KOH/K_2CO_3 have a higher etch rate for the 5-sec intervals relative to the measurements at 30-sec intervals. This is an indication that dissolution of the etch product from the surface is still a limiting factor with the KOH/K_2CO_3 etchants although there is an overall enhancement in the etch rate with these solutions.

Table I Activation Energies (Kcal/Mol)

Etch Interval (sec)	8.6*M* KOH	6.7*M* KOH/2.4*M* K_2CO_3
5	11.7	10.1
30	13.2	12.7

CONCLUSIONS

A 6.7*M*/1.9*M* KOH/K_2CO_3 solution has a 40–50% faster etch rate at 5- and 30-sec exposures compared to a 6.7*M* KOH solution. The faster etch rate, along with the visual observation of a thinner gel layer

and less flocculant etch by-product in solution, suggests that the K_2CO_3 additive enhances the dissolution of the hydrolyzed polyimide. As the K_2CO_3 concentration is increased, the etch rate increases when the KOH concentration is maintained at $2.7M$. The maximum in etch rate observed at $1.9M$ K_2CO_3 when the KOH concentration was held at $6.7M$ probably results from solubility limits.

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Received September 10, 1990
Accepted December 21, 1990