

Chemical Etching of Polyimide Film

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SYNOPSIS

Chemical etching rates of BPDA/PDA/ODA/BMI polyimide film by an alkaline etching solution with the presence of different kinds of etchants were studied by film-thickness measurement and UV absorption spectroscopy of dispersible etching residue. The etching rate of polyimide film in alkaline ethylene diamine solution is highest among the etching solutions studied in the present experiment. If an external bias voltage was applied during etching, the etching rate was increased. The effects of temperature, solubility of the etchant, and ultrasonic vibration on etching rate are also discussed. The presence of a radical in the process of etching reveals that the etching reaction is a type of radical chain reaction.

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INTRODUCTION

Because of their thermal and chemical stability, low dielectric constant, and ease of processing, polyimides have been found to be suitable materials for an interlevel dielectric in the production of electronic packaging materials.¹⁻⁶ In the process of manufacturing some microelectronic components, such as multilayer flexible printed circuit board or laminated interconnecters, it is required that the polyimide be etched, either to enhance its adhesive properties with respect to a deposited metal or to provide an electrical connection between various levels via holes.

Mechanical roughing of the polyimide surface by scrubbing with an abrasive slurry, by rolling, or by abrasive sandblasting does not abrade the surface uniformly, resulting in poor resolution of the printed circuit pattern. Dry etching of polyimide with an ion-beam, plasma,⁷⁻¹² or laser¹³⁻¹⁵ are other alternative methods employed. Wet etching of polyimide was disclosed by De Angeio¹⁶ using an ethylenediamine alkaline aqueous solution with an etching rate of 0.5 mil/h. Long etching time, degradation of the resist adhesion, and formation of nondispersible etching residue are drawbacks of etching by alkaline

solutions. A selective wet etching method was reported by Saiki et al.,¹⁷ providing a pattern with high-dimensional accuracy. An improved process of etching polyimide by adding a reactive material, such as aluminum metal, to an acidic or alkaline etching solution was studied by Youlton.¹⁸ It was reported that the generation of nascent hydrogen could double the etching rate and disperse the etching residue. However, in the practical manufacturing process, the etching time needs to be shortened further in order to produce highly reliable electronic components.

The main purpose of this study was to discover an etching solution and etching process capable of etching polyimide film at a high rate and especially capable of etching polyimide film made of BMI. Also investigated were the kinetics and mechanism of the etching of polyimide film.

EXPERIMENTAL

The polyamic acid employed in this study was derived from biphenyl tetracarboxylic dianhydride/1,4-phenylene diamine/oxydianiline/bismaleimide (BPDA/PDA/ODA/BMI), 15% in *N*-methylpyrrolidone (NMP). The viscosity was 2200 cps.

The polyimide (PI) film was made by first coating BPDA/PDA/ODA/BMI polyamic acid on glass plate or metal (copper or platinum) strip and then

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was thermally imidized by heating the sample in air from room temperature to 65°C over a period of 1 h and then heated up to the following successive temperatures of 150, 250, and 350°C over a period of 1 h each, and, finally, maintained at 350°C for another hour. The thickness of the PI film was around 6 μm .

The thermal stability of the PI film was studied using a thermogravimetric diagram (TGA) and differential scanning calorimetry (DSC), employing a Perkin-Elmer Model TGA 7 thermogravimetric analyzer and a Perkin-Elmer Model DSC 7 differential

scanning calorimeter in N_2 at a 10°C/min heating rate.

The PI film was etched in an alkaline etching solution of dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), ethylenediamine (EN), ammonia, or some other amines (Table I). Because of the common ion effect, less concentrated alkaline solutions allow more amine etchant to go into solution, with the converse also being true. In the present study, the concentration of sodium hydroxide was kept at 2M unless otherwise stated.

In the process of etching, the PI radical was mon-

Table I Etching Rate of PI/Pt and PI/Cu

Etching Solution	Temp (°C)	Ultrasonic Stir	External Voltage (V)	Current	Etching Rate ($\mu\text{m}/10 \text{ min}$)
2M NaOH	25	Yes	-1.8	108-238 mA	Negligible
	60	Yes	-1.8	162-674 mA	Very small
2M NaOH + 50% NMP	25	Yes	-1.8	12.7-18.9 mA	Small
	25	None	-1.8	14.2-21.3 mA	Small
	25	Yes	None		Negligible
	25	None	None		Negligible
2M NaOH + 50% DMF	25	Yes	-1.8	10-25.2 mA	Negligible
	60	Yes	-1.8	52-144.6 mA	Small
	60	Yes	None		Negligible
EN	25	Yes	-1.8	26-36 μA	Very small
	25	None	-1.8	31-42 μA	Negligible
	25	Yes	None		Negligible
	25	None	None		Negligible
	60	Yes	-1.8	24-60 μA	1
	60	None	-1.8	19-48 μA	1
	60	Yes	None		Small
	60	None	None		Small
2M NaOH + 28% NH_3	20	Yes	-1.8	87.8-208 mA	Small
	25	Yes	-1.8	100-250 mA	1.5
	25	Yes	None		0.5
	60	Yes	-1.8	131-513 mA	1
2M NaOH + 50% EN	30	Yes	-1.8	15.5-28.1 mA	1
	30	Yes	None		0.5
	40	Yes	-1.8	34.7-82.1 mA	2.0
	40	No	-1.8	35.1-87.9 mA	2.5
	50	Yes	-1.8	61-137 mA	3.5
	50	No	-1.8	54.3-126 mA	3-3.5
	60	Yes	-1.8	36-97 mA	5
	60	No	-1.8	42-155 mA	5.25
	60	Yes	-3	216-409 mA	9
	60	Yes	-5	42-155 mA	6.5/5 min
	70	Yes	-1.8	183-246 mA	8/5 min
	70	No	-1.8	198-261 mA	7/5 min
	80	Yes	-1.8	179-353 mA	8/3 min
	80	No	-1.8	132-218 mA	> 6/5 min

(Continued)

Table I (Continued)

Etching Solution	Temp (°C)	Ultrasonic Stir	External Voltage (V)	Current	Etching Rate ($\mu\text{m}/10 \text{ min}$)
2M NaOH + saturated EDTA	25	Yes	-1.8	9.1-25.1 mA	Negligible
	25	Yes	None		Negligible
	60	Yes	-1.8	40.7-106.3 mA	Very small
2M NaOH + 50% hexylamine	25	Yes	-1.8	63-110 mA	Very small
	25	Yes	None		Negligible
2M NaOH + 50% triethylamine	25	Yes	-1.8	22-34 μA	Negligible
	25	Yes	None		Negligible
2M NaOH + 50% dipropylamine	25	Yes	-1.8	19-30 μA	Negligible
	25	Yes	None		Negligible
2M NaOH + 50% EN on PI/Cu	60	Yes	-1.8	62-157.4 mA	3.5
	60	Yes	-1.94	79-224 mA	3.5

itored by a Bruker Model ER 200D 10/20 EPR spectrometer. The etching rate was studied at temperatures that varied from 25 to 80°C by measuring the thickness difference of the PI film before and after etching or by UV spectroscopy of dispersible etching residue when the etching rate was low. The thickness of the PI film was measured with a digimatic micrometer from Mitutoyo. The UV spectra were obtained from a Model DU-65 spectrophotometer. To investigate the effect of stirring on the etching rate, the etching solution was agitated in an ultrasonic bath. The reduction potential of the PI film was studied by taking the voltammogram of PI/Pt or PI/Cu laminate as a working electrode in an etching solution with a PAR 273 potentiostat/galvanostat equipped with a 270 programmer. The reference electrode was a saturated calomel electrode. The counterelectrode was a platinum electrode. A negative bias voltage of -1.8, -3.0, or -5.0 V (vs. platinum electrode) was stepped to the PI/metal laminate to study the effect of external voltage on the etching rate.

RESULTS AND DISCUSSION

Properties of Polyimide Film

The IR spectrum of imidized BPDA/PDA/ODA/BMI PI film prepared on glass is shown in Figure

1. The thermal stability curve obtained by TGA for PI film prepared on glass is shown in Figure 2. The TGA thermogram showed that the PI film is stable to near 425°C because of incorporation of BMI in the polymer backbone, which is more stable than those without BMI.¹⁹ The glass transition temperature studied by detecting the enthalpy change with DSC shows that incorporation of BMI in the polymer backbone lessens the rotational freedom and increases the energy barrier for rotation, resulting in a high T_g ($\sim 425^\circ\text{C}$). Besides, this type of PI film is more chemically stable than are those without BMI and need more severe conditions to etch.

Etching of Polyimide Film

Because of the high dielectric constant of water which can absorb microwaves, the EPR signal is very difficult to be observed in an aqueous solution. However, the signals of free radicals were observed when PI/Pt or PI/Cu laminate was etched in an alkaline etching solution of NMP or EN. When the temperature of the etching solution was below 60°C, the etching rate was slow and only one small broad peak of the EPR signal was observed [Fig. 3(a)], which was expected to be the signal of PI radicals because the g value estimated was the same as in the previous report ($g = 2.0038$).²⁰ When the temperature of the etching solution was around 80°C, the etching rate was much faster; meanwhile, several

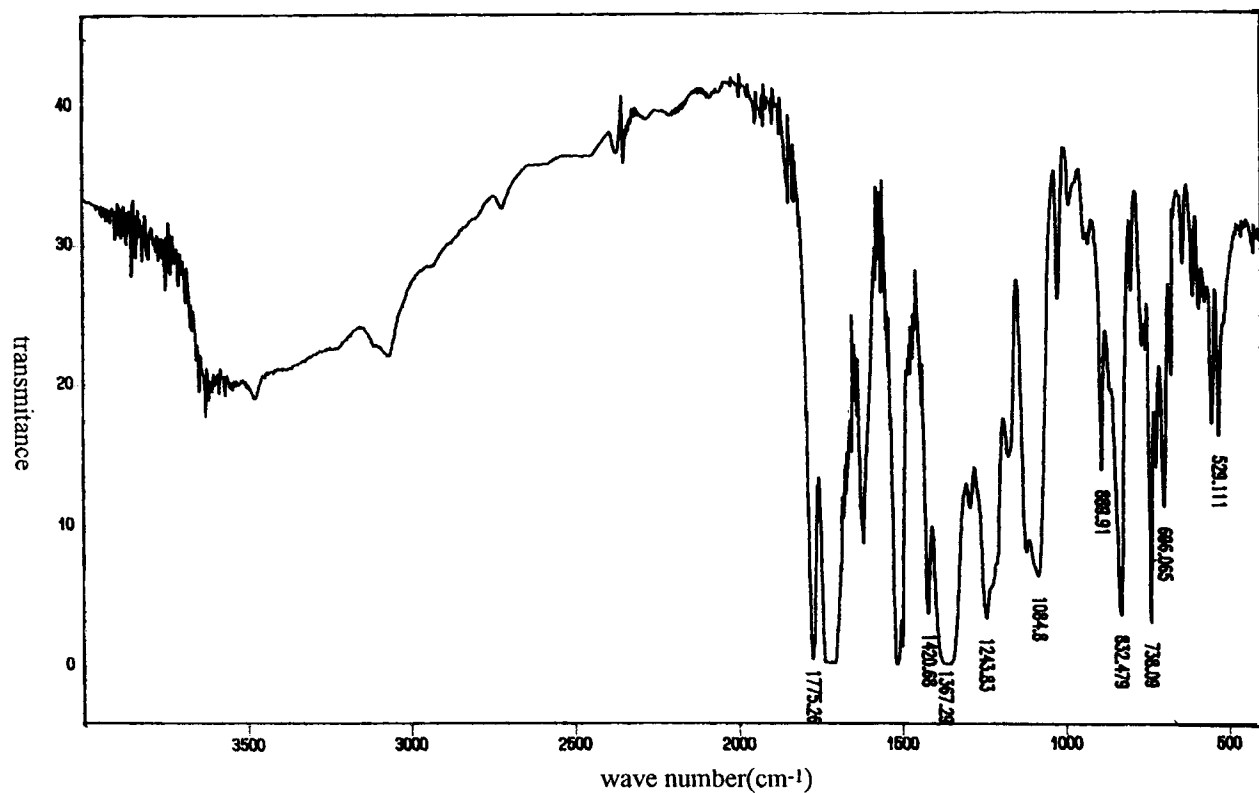


Figure 1 IR spectrum of imidized PI film.

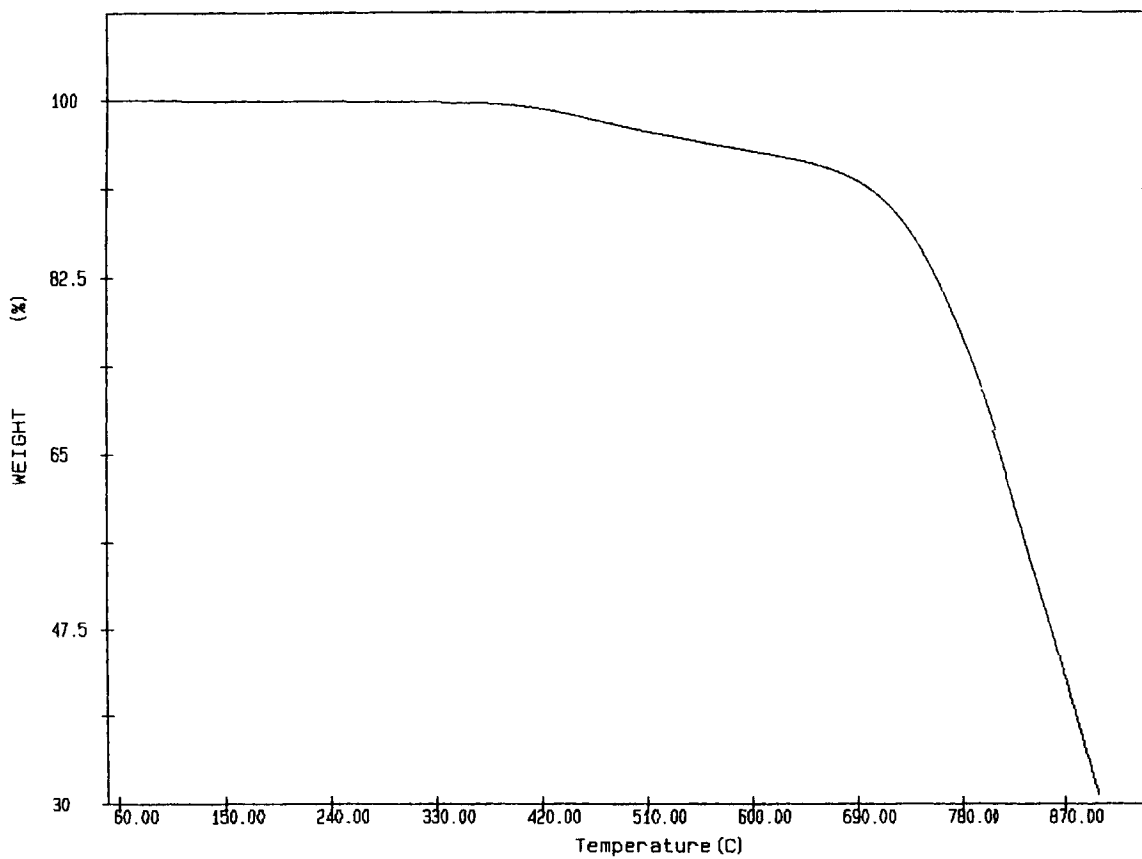


Figure 2 Thermal stability curve of PI film.

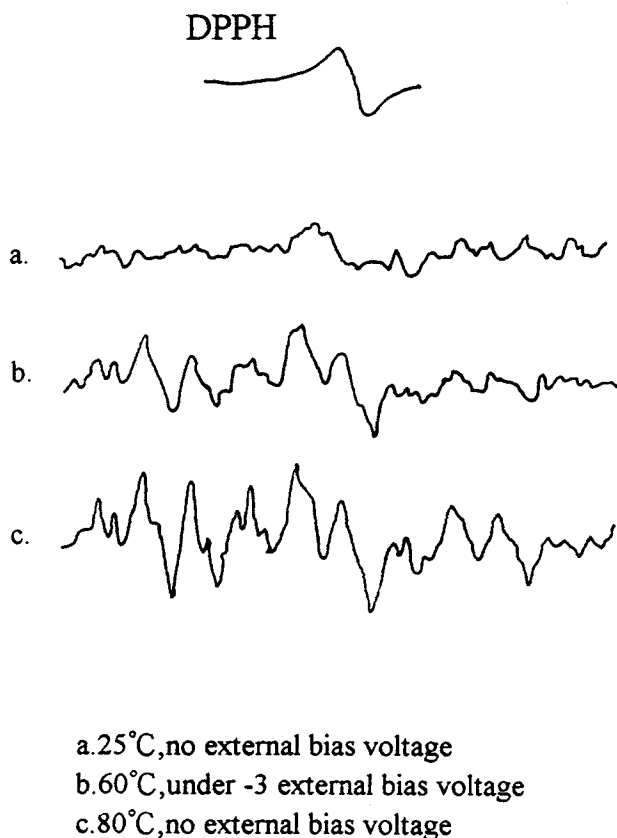


Figure 3 The EPR spectra of PI/Pt in 2M NaOH + 50% EN.

small sharp peaks of the EPR hyperfine splitting signal were observed [Fig. 3(b)]. The presence of radicals during etching indicates that the etching reaction is a type of radical chain reaction.

Effect of Temperature on Etching Rate

The etching rates of PI films are listed in Table I. It is found that temperature, concentration, and the nature of the etchant are the main factors that influence the etching rate of PI film. In general, the etching rate of PI is higher at higher temperature. But the etching rate did not vary much when the temperature of the etching solution was below 60°C. At temperatures above 60°C, the etching rate increased drastically with temperature. However, the reaction follows the kinetics of transition-state theory due to the fact that the logarithm of the etching rate in an EN alkaline solution and $(-1/T)$ are approximately linear in the temperature range of the present study (Fig. 4).

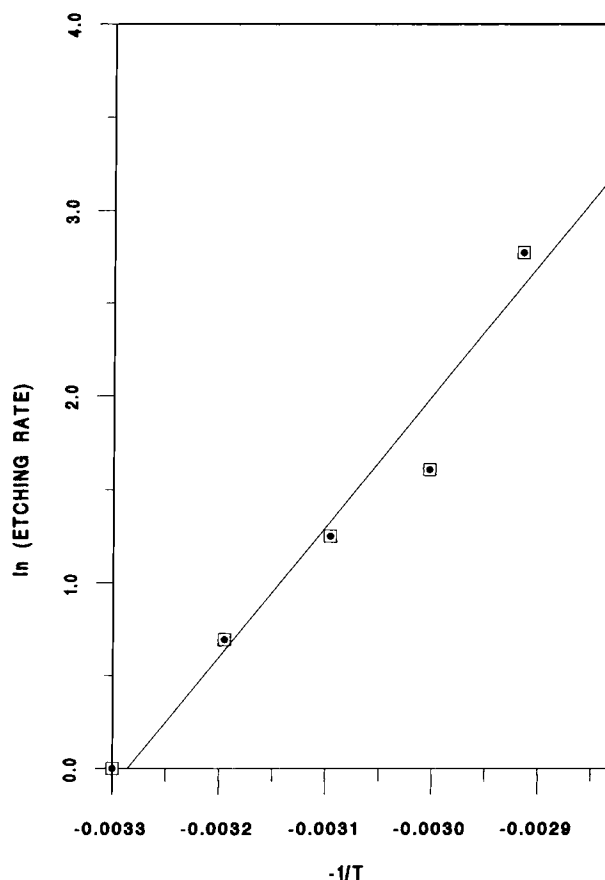


Figure 4 Variation of etching rate with temperature in 50% EN alkaline etching solution.

Effect of Etchant on Etching Rate

The etching rates of PI films are influenced by the kinds of etchants present in the etching solutions as shown in Table I. The etching rates of PI film in a 2M NaOH solution is negligible except at high temperature, and the etching rate in an EN solution is 1 $\mu\text{m}/10$ min at 60°C. However, the etching rate in a 2M NaOH alkaline EN solution is much higher

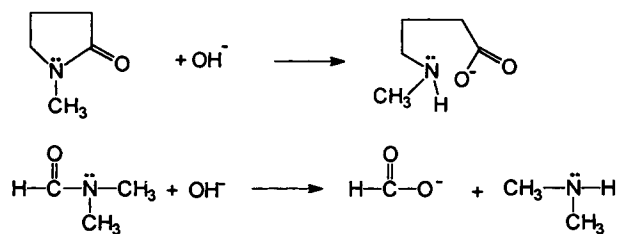


Figure 5 Hydrolysis of DMF and NMP in alkaline solution.

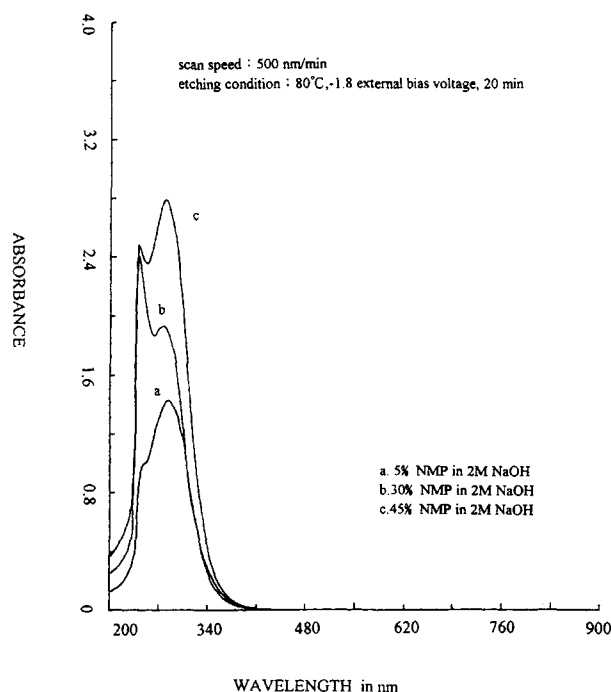


Figure 6 Effect of NMP concentration on etching rate.

($\sim 5 \mu\text{m}/10 \text{ min}$) at 60°C due to the synergistical effect of the alkaline solution and EN. Also, the etching rate of PI in alkaline solutions of EN is much higher than those with other amine etchants of triethylamine, *N*-hexylamine, or dipropylamine due to better solubility of EN in an alkaline aqueous solution.

Although the solubility of DMF is high in an alkaline aqueous solution, its incorporation does not influence the etching rate either at room temperature or at 60°C . Such a phenomenon may be due to the hydrolysis of DMF in an alkaline solution, resulting in the cleavage of the C—N bond and producing dimethylamine (Fig. 5),²¹ which is very volatile (bp 7.4°C).

The solubility of ammonia in an alkaline aqueous solution is also rather high, but ammonia is volatile, resulting in an ammonia alkaline solution with a moderate etching rate ($1.5 \mu\text{m}/10 \text{ min}$ at 25°C , $2.0 \mu\text{m}/10 \text{ min}$ at 60°C). The etching rate of NMP is comparable with an ammonia alkaline solution if the NMP etchant is mixed with a sodium hydroxide solution at 80°C for 40–60 min prior to use to get a homogeneous one-phase solution, and the etching rate is higher in a more concentrated solution as shown by the UV spectra of a dispersible etching residue (Fig. 6). Hydrolysis of NMP in an alkaline solution at high temperature (80°C) results in the formation of a secondary amine (Fig. 5). Free rad-

icals were observed by EPR spectroscopy when a homogeneous one-phase solution is formed. It was speculated that the etching ability of an NMP alkaline solution was enhanced by the generation of free radicals in the process of hydrolysis of NMP because there was no signal of a free radical observed for an extended hydrolyzed ($>6 \text{ h}$) NMP alkaline solution and the etching ability of such a solution was decreased. The etching rate of an NMP alkaline solution is low if the solution is mixed at 60°C with too few free radicals to be observed by EPR spectroscopy. However, a homogeneous one-phase solution will also be formed after 10 h of mixing. If NMP was mixed with an alkaline solution at a temperature lower than 60°C , it is very difficult to get a homogeneous one-phase solution, and the etching rate is very low (negligible).

Ethylenediamine tetracetic acid (EDTA) is a tertiary amine and the etching rate in an EDTA alkaline solution is very low. The results of the present study show that an alkaline solution with a concentrated EN etchant is a high etching rate solution for PI film.

Effect of Agitation

In general, the etching rate of PI is increased in an ultrasonic bath for all etchants at high temperature (Table I and Fig. 7). Among the etchants studied,

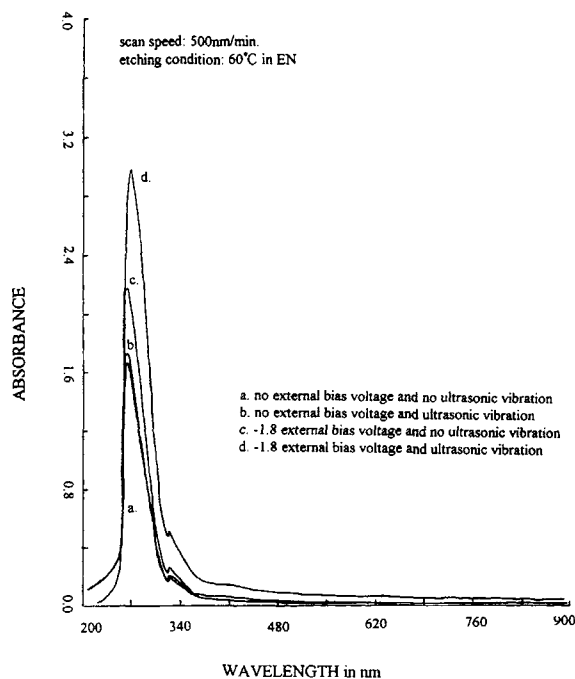


Figure 7 UV spectra of dispersible etching residue.

the etching rate of an EN alkaline solution at 80°C is at least doubled with ultrasonic vibration.

Based on the synergistic effect of sodium hydroxide and EN and the results of present experiment, it is speculated that the first step in the etching of PI is the opening up of the crosslinking network of PI by amine. The swelled sites are then etched by an alkaline solution. Agitation assists the dispersion of the etching residue in the solution and the penetration of the amine into PI film for further expansion of polymer network.

Effect of External Bias Voltage

One important characteristic of PIs is their ability to undergo a redox reaction in electrolytic solutions.²²⁻²⁴ When a constant potential of -1.8 V (vs. Ag/AgNO₃) was applied to PI/Pt electrode in non-aqueous electrolytic acetonitrile solution, a PI radical was observed by EPR spectroscopy.²⁰

In the present experiment, the reduction potential of PI to the PI radical was investigated by scanning from the equilibrium potential of PI/Pt or PI/Cu laminate in an etching solution toward a more negative voltage until a significant reduction peak was

observed. The voltammograms thus obtained are shown in Figure 8. The reduction potential of PI film interfaced with copper was more negative than was the film interfaced with platinum. Also, the etching rate was lower when interfaced with copper than when interfaced with platinum if the other conditions were the same (Table I).

The rate of etching increased when an external bias voltage more negative than the reduction potential of PI film was applied during the etching (Table I and Fig. 7). Also, in general, for the same etchant, the etching rate was higher with a higher current recorded at the external bias voltage. If an external bias voltage was applied during the etching of the PI/Pt laminate in an alkaline etching solution of NMP or EN at high temperature (~80°C), several small peaks of the EPR hyperfine splitting signal was also observed [Fig. 3(c)], which was similar to the peaks observed without external voltage. The signal decreased when the external voltage was turned off again, indicating that the free radical was rather reactive and a coupled chemical reaction followed right after the free radical was formed, which might result in the further degradation of the PI film. The detailed processes of the etching reaction mechanism need further investigation.

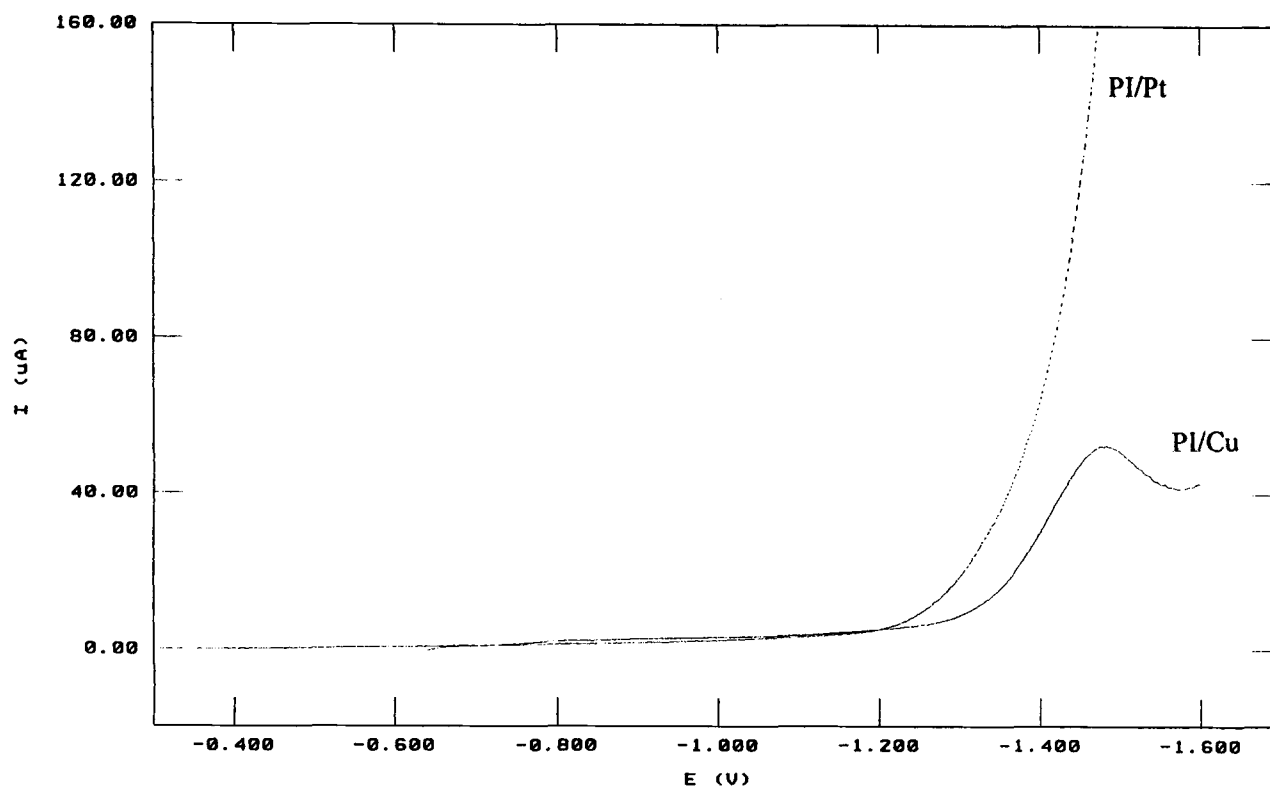


Figure 8 The voltammograms of PI/Pt and PI/Cu in 2M NaOH + 50% EN etching solution at 60°C.

CONCLUSION

The following conclusions are drawn based on the results of our studies:

1. An alkaline solution with a concentrated amine etchant, such as ethylenediamine, will result in a high etching rate of PI film.
2. Alkaline solutions with volatile etchants, such as ammonia or dimethylamine (from the hydrolysis of DMF) have a relatively low etching rate.
3. The etching rate for an alkaline solution with less soluble etchants, such as triethylamine, *n*-hexylamine, or dipropylamine, are even lower.
4. Ultrasonic vibration can increase the etching rate, especially at high temperature.
5. The etching reaction is a type of radical chain reaction because free radicals were observed in the process of etching.
6. The reaction follows the kinetics of transition-state theory because the graph for the logarithm of the etching rate in an EN alkaline solution and inverse temperature are linear.
7. If an external bias voltage more negative than the reduction potential of PI film was applied, the etching rate would increase.

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