Adverse Chemical Effects on the Plasma-Deposited Amorphous Silicon Carbide Passivation Layer of Thermal Ink-Jet Thin-Film Heaters

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A study of the kogation/etching behavior of thermal ink-jet thin-film heater devices passivated by a plasma-deposited amorphous hydrogenated silicon carbide (α-SiC:H) layer shows that some of the chemicals found in inks suffer thermal decomposition during device operation and deposit the decomposition products onto the heaters (kogation), others are responsible for etching of the heater passivation layer, and some are responsible for both kogation and etching. Those chemicals responsible for kogation include amines, both aliphatic and aromatic (i.e., aniline), and their alkylated homologues. Etching is primarily due to either high pH (HO$^-$) or radicals (i.e., HO$^•$). Kogation is theorized to arise from several thermally activated sources. Chemicals at concentrations of 0.1% or lower can be the major source of the kogation or etching.

Introduction

Thermal ink jet, also known as bubble jet (BJ), repeatedly heats the ink by electrical pulses of a few microseconds duration passing through small thin-film heaters to form a vapor bubble that ejects the ink through nozzles. A schematic representation of a typical thermal ink jet device is shown in Figure 1.

Whereas BJ suffers from the same limitations of other ink jet technologies, it is unique in its problems of kogation and etching, either of which can lead to rapid heater destruction, i.e., a "hard" failure, or poor performance, i.e., a "soft" failure. The term "kogation" was coined[1,2] to indicate products of thermal decomposition of ink ingredients and the subsequent deposition of these products on top of BJ thin-film devices.[1,3-6] Several remedies for kogation have been suggested in the literature[7-9] including careful selection of all ink ingredients, especially the dyes. However, the problem of etching has been largely ignored until very recently when it was revealed as a major source of "hard" failure.[3,4,6]

We have studied these phenomena by individually examining the ink components in an attempt to separate some of the variables. The rationale is simple: even the simplest dye has a complex structure with many functional groups; in addition, the interaction of ink components can be complicated. Therefore, the study begins by the examination of unique ink components; if the ink component is complicated with several functional groups, as are most dyes, then we examine each functional group individually.

We consider both inorganic and organic chemicals. Within the realm of inorganic chemicals, we examined the effect of typical salts found in aqueous inks and the effect of pH; some of these results have been reported recently.[10,11] For the organic effects, we study benzene rings substituted with one of those functional groups typically found in water-soluble dyes, progress of polyfunctional model compounds and mixtures, and finally move on to relatively simple, representative dyes.

Experimental Section

The testing procedures are essentially the same as described previously.[3] The topmost overcoat of the devices is amorphous hydrogenated silicon carbide (α-SiC:H) made from methane and argon-diluted silane in a plasma-enhanced chemical vapor deposition process. The ratio of silicon to carbon is between 0.9 and 1.1, the hydrogen content is 20–30 atom %, and the oxygen content is about 1–2 atom %. There is a second dielectric layer of amorphous hydrogenated silicon nitride between α-SiC:H and the resistor. The behavior of this nitride layer is not specifically studied. Note also that sputter-deposited tantalum is nowadays often used on top of carbide. The failure of this tantalum layer is, however, reported elsewhere.[12]

The printheads are mounted such that individual jet streams can be monitored by a synchronized video camera connected to a video recorder. In this way we are able to determine the actual jetting time and avoid the potential detrimental "dry heating", which is explained below. The heaters are typically driven by dc pulses at 2 kHz, such that surface temperature reaches a maximum of 400 °C at the end of the pulse. It is conceivable that overdriving the heater may increase the rates of etching and kogation greatly. However, the effect of driving voltage or surface temperature is not reported here.

Results and Discussion

The kogation/etching of all of the samples is given in Table I. Unless otherwise noted, the concentration of the test species is 5 wt %. Etch rates are given in angstrom per megapulse (Å/Mp). The last column of Table I contains any comments on that sample. The structures of the more complex chemicals used in this study are given in Figure 2.

Fluid Vehicle. We use 50% ethylene glycol (EG) solutions (1, Table 1) in water as the test vehicle, and only a small amount of kogation is produced by this solution by itself. If solutions with less glycol are used, the detrimental event of "dry heating" may be encountered; even with 50% EG we still need to nonitor the tests by video

(1) Ikeda, M. The Bubble Jet Printing Technology for BJ-80 Printer. IGC 18th Annual Conference on Ink Jet Printing, Amsterdam, Mar 1985.

(2) Hackleman, D. *Hewlett-Packard J.* 1985, *36*, 32.

(3) Chang, L. S. *Electrophotography* 1989, *28*, 2–9.

(4) Chang, L. S.; Olive, G. *Proc. Soc. Inform. Display* 1987, *28*, 477–482.

(5) Askeland, R. A.; Childers, W. D.; Sperry, W. R. *Hewlett-Packard Jl.* 1988, *39*, 28–31.

(6) Chang, L. S. *Proc. Soc. Inform. Display* 1989, *30*, 57–63.

(7) Suga, Y.; Eida, T.; Koike, S.; Ohta, T. Dyes for Bubble Jet Inks. *The Fourth International Congress on Advances in Non-Impact Printing Technologies, Advance Printing of Paper Summaries*; The Fairmont Hotel, New Orleans, LA, sponsored by the SPSE; Mar 20–25, 1988; pp 123–126.

(8) Kobayashi, H.; Koumura, N.; Ohno, S. US Patent 4,243,994.

(9) Jpn. Kokai Tokkyo Koho JP 58/174,470, to: Canon, K. K. *Chem. Abstr. 100*, 211856e.

(10) Chang, L. S.; Gendler, P. L. Chemical Effects in Ink Jet Thin-Film Heater Breakdown; 63rd Colloid and Surface Science Symposium; Seattle, WA, June 18–21, 1989; sponsored by the American Chemical Society.

(11) Chang, L. S.; Gendler, P. L.; Jou, J.-H. *J. Mater. Sci.* 1991, *26*, 1882–1890.

(12) Chang, L. S.; Eldridge, J. M.; Dunton, V. 176th ECS Meeting; Hollywood, Florida, October 1989.
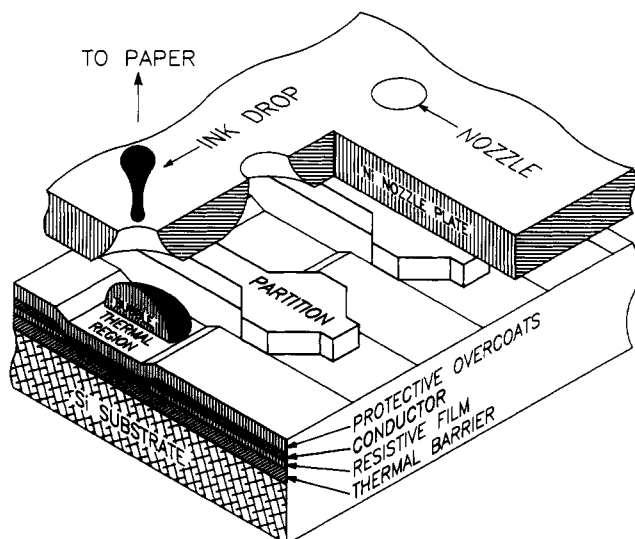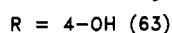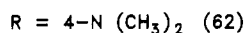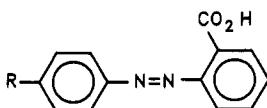
Figure 1. Typical thermal ink-jet device schematic.

CHEMICAL STRUCTURES[*]

R–ϕSO$_3$M

R = H, M = Na (27)

R = 4–CH$_3$, M = Na (28,29)

R = 4–CH$_3$, M = N(CH$_3$)$_4$ (30)

ϕOH (43,44)

(46)

ϕNR$_2$

R = H (39,40)

R = CH$_3$ (41)

(45)

HO–CO$_2$Na (49)

R–N=N–SO$_3$H

R = 4–H (58)
R = 4–ϕNH (59)
R = 4–N(CH$_3$)$_2$ (60)
R = 2,4–(OH)$_2$ (61)

R–N=N– (CO$_2$H)

R = 4–N (CH$_3$)$_2$ (62)
R = 4–OH (63)
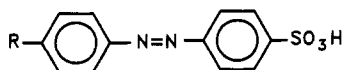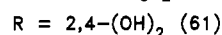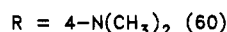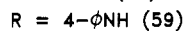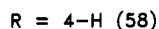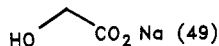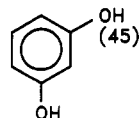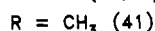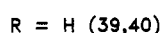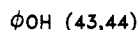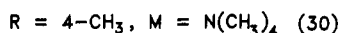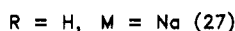
*Numbers in parentheses refer to Table I entry.

Figure 2. Chemical structures.

to avoid that pitfall. The term "dry heating" refers to the situation where jetting of a test liquid has ceased but heaters are still being pulsed. Because of the poor thermal diffusivity of air, heater temperature rises significantly higher, and accelerated etching and/or kogation caused by nonvolatile ingredients or previously deposited insoluble residues may occur. Thus dry heating was avoided whenever possible.

Etching of Various Inorganic Salts. All water-soluble dyes contain varying amounts of salts unless special measures are used to remove them. The two most common are NaCl (2–6) and Na$_2$SO$_4$ (7).

As shown in Figure 3, a log–log plot, the etch rate of NaCl doubles for every factor of 10 increase in chloride
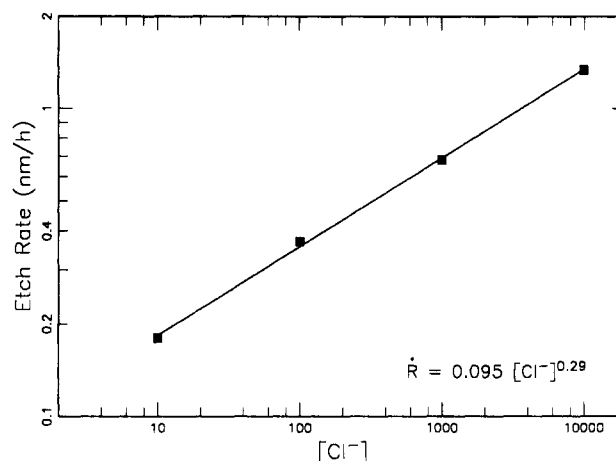
Figure 3. Etch rate of sodium chloride.
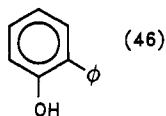
ion concentration. The slope of 0.287 indicates a complex dependence of the etch rate on the concentration of chloride. Numerous possibilities exist including electrochemical corrosion.

Dry heating is very corrosive during tests of NaCl solutions, and in most cases extremely severe etch rates would be observed if the data were to include that for dry heating. In fact, the 10000 ppm NaCl solution was very difficult to keep jetting; it seemed to stop often and enter the dry heating mode.

Several other salts were examined as the cations and anions were varied with the following conclusions available for etching of various salts:

Cations: (A) Neither sodium nor lithium is a vigorous etchant. (B) Quaternary alkylammonium salts (30, 31) suffer from a great deal of kogation, contradicting the literature,[13] presumably because a different heater surface (i.e., tantalum) was involved in that work.

Anions: (A) Fluoride (11) is a vigorous etchant. (B) borate (12) and phosphate (13) are vigorous etchants. (C) Sulfate (7) is a moderate etchant. (D) Chloride (2–6) etches more than bromide (14) or iodide (15), but all are relatively low-to-moderate etchants. (E) Sulfite, SO$_3^{2-}$ (16) appears to be a vigorous etchant (although the pH of 9.66 is high, as discussed in the next section), while metabisulfite S$_2$O$_5^{2-}$ (17) is not. (F) Azide, N$_3^-$ (18), is a moderate etchant, and this precludes its intended use as a biocide.

Effect of pH. The α-SiC:H passivation layer was chosen for its high chemical resistance, excellent wear resistance, and high thermal conductivity.[14,15] However, under proper conditions it can be vigorously attacked.[16] The effect of pH (19–26) is shown in Figure 4 and also plotted is the solubility of α-SiO$_3^-$ as a function of pH.[17] Figure 5 shows the amount of etching plotted against test cycles for solutions of pH from about 8 to 12. The fact that a linear relationship is obtained in each case suggests that the PECVD carbide is etched through a total dissolution process. One mechanism of etching, derived from these observations, is as follows: a thin layer of silicon

(13) Askeland, R. A.; Kappele, W. D.; Pawlowski, N. E.; Stoffel, J. L. Dyes Containing Tetramethylammonium Cation For Ink-Jet Printing Inks. US Patent 4,761,180, Aug 1988.

(14) Nishino, S.; Ibaraki, A., Matsumami, H.; Tanaka, T. *Jpn. J. Appl. Phys.* **1980**, *19*, L353-356.

(15) Muench, W. V.; Hoeck, P. *Solid State Electron.* **1978**, *21*, 479-480.

(16) Kern, W.; Deckert, C. A. In *Thin Film Processes*, Vossen, J. L., Kern, W., Eds.; Academic Press: New York, 1978; Chapter V-1, Chemical Etching, pp 430, 451.

(17) Alexander, G. B.; Heston, W. M.; Iler, R. K. *J. Phys. Chem.* **1974**, *58*, 453-455.
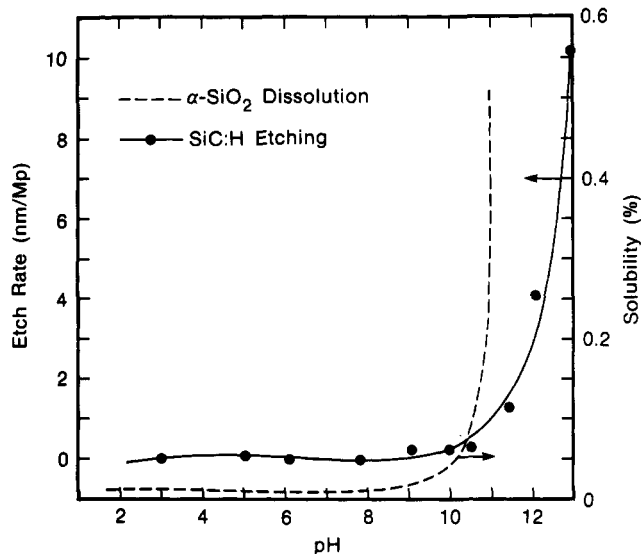
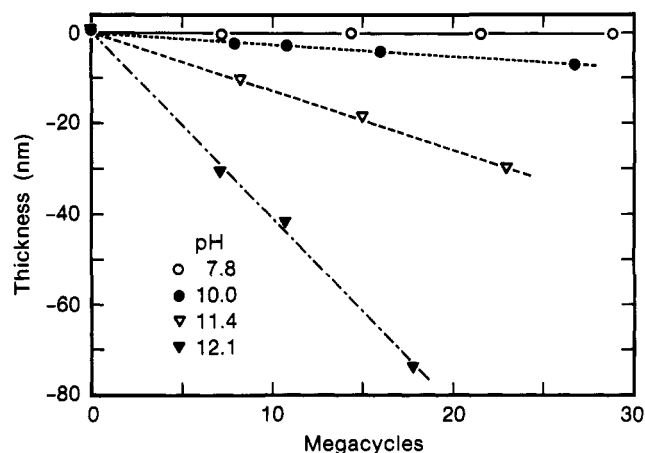**Figure 4.** Etch rate of α-SiC:H and solubility of silicate vs pH.

Figure 5. Etch rate of solutions of pH 8–12.

oxide is initially present on the silicon carbide. It is attacked and dissolved by hydroxide which strips the protective oxide layer, thus layer bare additional carbide. A new oxide layer forms from the exposure of the α-SiC:H to heat and air/water, and the process begins again. This mechanism, as it pertains to etching by carboxylate salts as model compounds, is discussed further in the section on the mechanism of etching.

Organic Model Compounds. The typical organic water-soluble azo dye of any color would contain one or more of the following chemical species: aromatic ring, sulfonate, carboxylate, at least one electron-donating group such as an amine or a phenolic OH, and, of course, the azo group. The majority of these functional groups from a typical aqueous azo dye occur on an aromatic ring, and the model compounds for these are therefore the phenyl derivatives of the aforementioned functional groups.

Benzenesulfonic acids and their salts: The most common water-solubilizing groups are the sulfonates. The model compounds are therefore the sodium salts of benzenesulfonic acid (27) or tosic (toluenesulfonic) acid (28, 29), and they have low-to-moderate etch rates and little-to-some kogation. As noted above, tetramethylammonium tosylate (30) has increased etch rate and enormous amounts of kogation.[18] In addition, this example has a
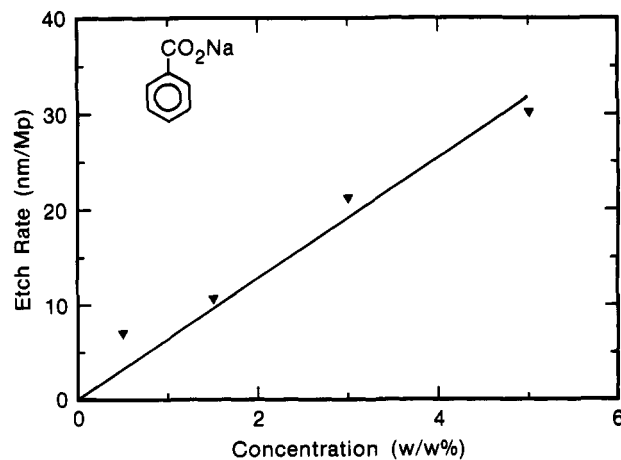
Figure 6. Etch rate of sodium benzoate vs concentration.

kogation layer invisible under an optical microscope, as suggested by the profilometer scan, which indicates that mere optical inspection as evidence for kogation[7] has to be done with caution.

Carboxylic acids and their salts: The second most common water-solubilizing group is the carboxylic acid. The model compounds examined began with salts of benzoic acid. The etching behavior of sodium benzoate was very severe, and the test was repeated several times at several concentrations (32–36), with the results shown in Figure 6; the response is linear with concentration.

Aliphatic acids studied for etching include acetic and propionic acids. The etch rates of sodium acetate (37, 40 Å/Mp) and sodium propionate (38) are similar to that of benzoate.

Anilines: Aniline itself (39) does not etch but shows moderate-to-severe kogation and some crystalline decomposition products. Aniline hydrochloride (40) has severe kogation and some etching, and N,N-dimethylaniline hydrochloride (41) has severe kogation and unknown etching since the kogation could not be removed by simple physical methods.

Phenols: Phenol itself at slightly acidic (43) or neutral (44) pH does not etch or kogate. The neutral solution was attained by the addition of NaOH. Other phenols including resorcinol (1,3-dihydroxybenzene, 45) and 2-phenylphenol (46), sold by Dow Chemical as a biocide under the trade names Dowicide-1 or Dowicide A for the sodium salt, are similar to phenol.

Peroxide as an Etchant. Dilute solutions of hydrogen peroxide proved to be vigorous etchants (47, 48). The data indicates that the etch rate is directly proportional to concentration. As discussed in the mechanism of etching below, the ultimate species responsible for etching could be an OH radical and not necessarily an OH anion. One variable is the presence of the EG, which under the test conditions might be oxidized to glycolic acid and this might be the etchant in the peroxide solution.

To clarify this, an aqueous peroxide solution was prepared as well as an aqueous solution of sodium glycolate. The sodium glycolate solution (49) proved to behave much like acetic and propionic acid salts and is a vigorous etchant. The verification of etching by radicals thus fell to an aqueous solution of peroxide without any cosolvent. The etch rate[20] of both 1% (15 Å/M) and 0.1% (1.6 Å/M) aqueous hydrogen peroxide proved the point:

(18) Palmer, D. J. Process for Preparing Ink Compositions for Ink-Jet Printers; US Patent 4,685,968, Aug 1987.
(19) Eida, T.; Kobayashi, M. US Patent 4,435,717.

(20) A modified apparatus has to be used when no glycol is present due to the reduced viscosity. A blank was examined first, and it has an etch rate of <0.5 Å/MP; the etch rates of the two aqueous peroxide solutions were far enough above the blank to justify the conclusions.

Table I. Kogation/Etching of Miscellaneous Compounds/Mixtures

no.	compd	pH	10^3k, mho/cm	kogation	etch rate, Å/Mp	comments
1	50% EG/water	6.1	0.0016	some on heater	0	
2	50% EG/water with NaCl	6.25	0.20	none	4.3	gas observed while jetting
3	50% EG/water with NaCl	6.72	0.58	none	1.5	
4	50% EG/water with NaCl	7.17	2.3	some off	0.33	
5	50% EG/water with NaCl	6.32	4.9	some off heater	5.5	dry heating (DH) often present
6	50% EG/water with NaCl	6.65	18	none	4.6	
7	Na_2SO_4	6.6	0.54	none	5.2	uniform etching
8	LiCl (5%, 4180 ppm)	6.42	3.5	none	2.4	jetting stable
9	LiCl (1000 ppm)	7.07	1.04	some off	0.72	
10	LiCl (100 ppm)	7.1	0.10	none	0.23	
11	NaF (0.5%)	7.22	0.48	mod off	17.8	a heater failed at 1 h
12	boric acid (with NaOH)	7.15	0.74	none	16	
13	NaH_2PO_4 (1%)	7.20	5.0	some	14	1 heater failed by 4 h; etch rate = kt^a, $a > 1$
14	NaBr	6.78	14	none	1.0	
15	NaI	8.58	10	none	2.6	no DH; etches overcoat
16	Na_2SO_3 (0.5%)	9.66	1.6	mod off heater	14.9	
17	$Na_2S_2O_5$ (0.5%)	5.36	1.2	mod off heater	0.9	
18	sodium azide (1%)	8.34	4.2		4.2	
19	50% EG/water with NaOH	7.80	0.0024	some	0	
20	50% EG/water with NaOH	9.06	0.027	some on/off heater	2.5	
21	50% EG/water with NaOH	9.97	0.042	some on/off heater	2.5	
22	50% EG/water with NaOH	10.5	0.15	some on/off heater	2.9	
23	50% EG/water with NaOH	11.40		none	13	
24	50% EG/water with NaOH	12.07	9.1	none	41	
25	50% EG/water with NaOH	13		none	100	
26	50% EG/water with NaOH	13.9		none	550	
27	$PhSO_3Na$	7.40	6.2	little off heater	4.9	
28	p-CH_3PhSO_3Na	7.48	4.4	some off heater	3.6	
29	p-CH_3PhSO_3Na (1%)	7.02	1.1	little off heater	1.4	
30	p-$CH_3PhSO_3N(CH_3)_4$	6.89	3.0	severe on heater	6.5	kogation invisible under OM
31	p-CH_3PhSO_3H with $N(Et)_4OH$ (3%)	7.07	3.5	some off heater	2.7	
32	PhCOONa	6.81	6.0	none	30	
33	PhCOONa	6.76	5.6	mod off heater	25	
34	PhCOONa (1.5%)	7.11	2.65	none	10.5	
35	PhCOONa (0.5%)	7.17	1.0	none	6.9	
36	PhCOONa (3.0%)	7.03	8.8	none	20	
37	CH_3COONa	8.74			40	
38	C_2H_5COONa	7.19	4.98	some off heater	13	
39	$PhNH_2$	8.38		mod/severe on heater severe off heater	0	crystals formed; debris/corr on Ni plate
40	$PhNH_2 \cdot HCl$	5.01	1.8	severe off heater	1.7	Ni corroded; kogation filmlike and not removable
41	$PhN(Me)_2 \cdot HCl$	3.1		severe on/off heater; film ca. 2000 Å thick	unknown	
42	$H_2NPhN(CH_3)_2$ (1%)	6.67	3.1	some off heater edge	0	soln unstable
43	PhOH	4.92	0.0058	little off heater	0	
44	PhOH/PhONa	6.98	0.012	none	0	
45	resorcinol	5.60	0.0016	none	0	
46	Dowicide-1 (0.1%)			none	0.59	
47	HOOH (0.33%)			severe on,* some off	12.5	*local peak, not removable
48	HOOH (0.1%)	6.64	0.0011	some off	3.8	
49	Na glycolate	7.05	0.62	little	13 (av) or 24 (max)	
50	o-ClPhCOONa	6.89	4.8	severe on/off heater	2.8	
50a	o-ClPhCOONa	6.89	4.8	severe on/off heater	4.0	Cl up after test
51	m-ClPhCOONa	6.90	4.8	mod on/off heater	8	
52	p-ClPhCOONa	6.93	4.5	some on/off heater	10.4	
53	$ClCH_2CH_2COONa$	7.06	7.6	some off heater	2.8	
54	$CH_3CHClCOONa$	7.14	9.0	some off heater	0.3	
55	$PhOCH_2CH_2COONa$	7.06	5.0	some on/off heater	9.6	
56	CCl_3COONa	7.07	8.0	some to mod.	40	
57	$PhOCH_2COONa$	7.11	5.7	some off	6	
58	p-$PhN{=}NPhSO_3Li$ (1%)	7.03	1.6	500 Å @ 3 h	1.0	
59	$PhNHPhN{=}NPhSO_3$ (1%)	7.01	2.5	little	1.4	
60	methyl orange (1%)	8.82	0.71	1400 Å by 20 Mp	2.1	no DH
61	2,4-di-HOPhN= NPhSO_3LI	7.00	2.4	100 Å/Mp	0	
62	methyl red (0.1%)	7.01	.050	severe on/mod off	0.7	Li^+ salt
63	HABA (0.1%)	7.23	0.076	little on/off	0.8	

peroxide is a vigorous etchant, and OH radical, not OH^-, may be the ultimate etchant produced from thermal decomposition of carboxylic acids, among others, as discussed below.

Mechanism of Etching. A mechanism for the etching by hydroxide ion and species that are theorized to generate hydroxide ion, such as carboxylic acid salts, is given below. Carboxylate salts undergo decarboxylation to produce a
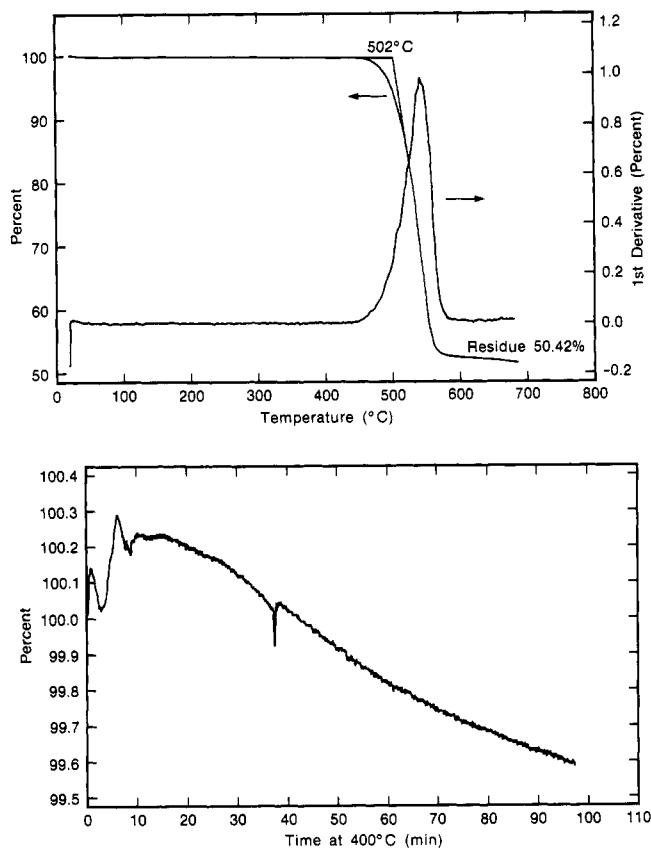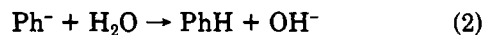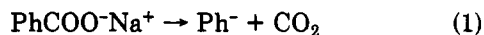
Figure 7. Top: TGA of NaOBz. Bottom: TGA of NaOBz held at 400 °C.

Figure 8. Auger analysis of heater surfaces.

carbanion, a very basic species, during the heating cycle of heater. After the heating cycle is over and the ink covers the heater again, the carbanion is quenched by water and produces hydroxide ion.

However, given the etching behavior of peroxide solutions, which are known to thermally generate radicals,[21] we cannot rule out that the etching in many instances is due to radicals. The steps for the hydroxide route to etching by carboxylate salts are shown in the following chemical equations:

$$PhCOO^-Na^+ \rightarrow Ph^- + CO_2 \qquad (1)$$

$$Ph^- + H_2O \rightarrow PhH + OH^- \qquad (2)$$

$$OH^- + \alpha\text{-}SiO_2 \rightarrow HSiO_3^{-2} \qquad (3)$$

To pursue this subject, we subjected NaOBz to thermogravimetric analysis (TGA) in dry nitrogen (Figure 7, top) and found it to decompose at about 500 °C; the use of ambient air in place of dry nitrogen gave the same results. Initially, this is puzzling since the maximum temperature of the ink jet device is supposedly less than 400 °C,[3] and yet NaOBz is a vigorous etchant. A few other attempts were made to more closely model the environment of the ink-jet device without any changes in results.

We held a sample of NaOBz on a SiC:H-coated silicon wafer at 400 °C for 90 min and found a very minor loss of weight, less than 0.5% (Figure 7, bottom). This suggests a very slow reaction is occurring and that only a very small percentage of any test compound actually decomposes. Another possibility is that perhaps the actual medium in
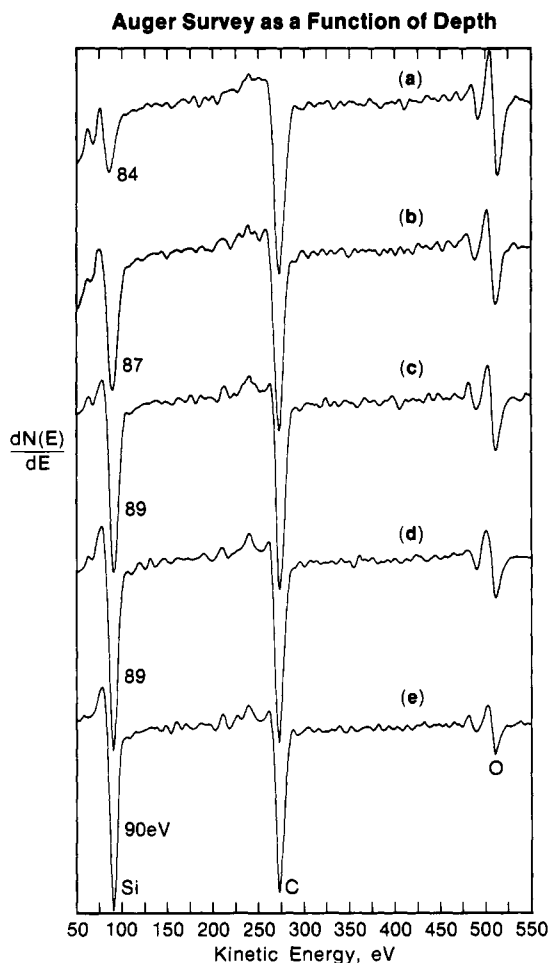
the device, namely, one saturated with water vapor, has a great deal to do with the processes.

An observation made with sodium 2-chlorobenzoate, as noted below, agrees with the above theory and is suggestive that only a very small percentage (i.e., <0.01%) of the compound undergoes decomposition. If this is true for all compounds, it would be very difficult to detect. This is consistent with the small weight loss of the sodium benzoate sample held at elevated temperature on the wafer for 90 min.

Auger Analysis: In an attempt to obtain some additional information with regard to the above proposed mechanism, we analyzed the surface of various heaters with Auger depth profiling. These heaters included those that were unused, those used but unetched, and those severely etched. If we could determine the extent of oxygen penetration into the heater or saw any difference in the profile of any of these, the mechanism would be incorrect. The results, shown in Figure 8, were the same for all of these kinds of heaters and indicate that there is only a thin layer of oxide, consistent with the proposed mechanism.

Difunctional Carboxylate Salts: Structural Modifications That Affect Etching. The vigorous etching of all simple carboxylate salts suggested a few ways to obviate this activity by taking advantage of the proposed mechanism, namely, a carbanion as an intermediate. If a carbanion was in fact an intermediate, then by proper modification of the structure, which would incorporate a group such as chloride that could be ejected in either an α- or β-elimination reaction, the etch rate ought to be reduced since we would be trading the relatively mild etch behavior of chloride anion for the vigorous etching of hy-

(21) Benson, S. W.; Shaw, R. Thermochemistry of Organic Peroxides, Hydroperoxides, Polyoxides, and their Radicals. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1970; Vol. 1, Chapter 2, pp 121-3.

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Table II. Kogation of Difunctional Carboxylate Salts

carboxylate salt kogation	Table I no.	Å/Mp	etch rate
1. benzoic	32–36	25–30	none
2. 2-chlorobenzoic	50	3–4	severe
3. 3-chlorobenzoic	51	8–9	moderate
4. 4-chlorobenzoic	52	10	moderate
5. propionic	38	13–18	some
6. 3-chloropropionic	53	3	some
7. 2-chloropropionic	54	0.3	some
8. 3-phenoxypropionic	56	10	some
9. acetic	37	40	none
10. trichloroacetic	56	33–45	none
11. phenoxyacetic	57	6	some

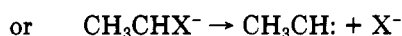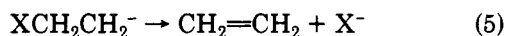droxide. The data are collected in Table II and support this hypothesis.

The chemical intermediates thought to account for both the decrease in etching and the increase in kogation are consistent with the above observations. In the case of the chlorobenzoic acids, 2–4 in Table II, chloride ion ejection will produce a benzyne intermediate. The presence of *o*-benzyne as an intermediate, from the 2-chloro isomer, is well established.[22] In addition, we determined the level of Cl⁻ before and after reaction by sampling the recycled test fluid and found an increase of about 10 ppm. This corresponds to about 0.01% elimination of chloride to form *o*-benzyne. The *o*-benzyne can undergo many subsequent reactions and probably accounts for the increased kogation.

The case of *m*- or *p*-benzyne is much more tenuous, and mechanistic proof for both of these is more elusive.[23,24] In addition, we found no change in the level of Cl⁻ before and after jetting for either the 3- or 4-chlorobenzoic acid, although the higher level of chloride in these acids would preclude the detection of small increases.
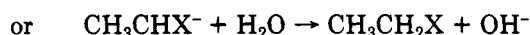
A similar case is found for the substituted propionic acids, 5–8 in Table II. In this case, decarboxylation gives an (substituted) ethyl anion, and its fate is determined by the nature of the substituent, as shown in reactions 4–6.

$$XCH_2CH_2CO_2^- \rightarrow XCH_2CH_2^- + CO_2\uparrow \qquad (4)$$

or $\qquad CH_3CHXCO_2^- \rightarrow CH_3CHX^- + CO_2\uparrow$

if X is eliminated

$$XCH_2CH_2^- \rightarrow CH_2{=}CH_2 + X^- \qquad (5)$$

or $\qquad CH_3CHX^- \rightarrow CH_3CH{:} + X^-$

is X is not eliminated

$$XCH_2CH_2^- + H_2O \rightarrow XCH_2CH_3 + OH^- \qquad (6)$$

or $\qquad CH_3CHX^- + H_2O \rightarrow CH_3CH_2X + OH^-$
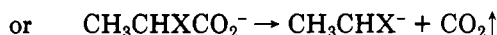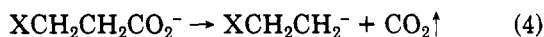
In this case, *β*-elimination of chloride is not as favored as the *α*-elimination, while *β*-elimination of phenoxide from 3-phenxoypropionic acid, Table II (8), did not occur given our detection limit of phenol (0.1 ppm) in the recirculated fluid.

Polyfunctional compounds and simple dyes: Two groups of water-soluble azo compounds were examined, one using the carboxylate group for solubility (62, 63) and the other using the sulfonate group for solubility (58–61). The dye methyl red (62) is soluble only at 0.1% by using the lithium salt. Even at this low level, the lithium salt of methyl red is both a severe kogater and a mild etchant. HABA (63), the analogue of methyl red where the dimethylamino group is replaced with an OH, is well be-

Table III. Auger Analysis of Typical Kogation

element	amt	element	amt
carbon	70	nitrogen	4.5
oxygen	6	sulfur	2.3

haved; these results were implied by the literature.[7] Similar results were obtained in the sulfonated series below.

We examined four simple water-soluble azo dyes in the sulfonate series, also at 0.1% loading and as the lithium salt. In this case the parent azobenzenesulfonic acid salt (58) has a low etch rate and some kogation; slightly more kogation is noted by the introduction of a *p*-aminophenyl group (59). The use of methyl orange (60), with a dimethylamino group, has much more serious problems, while a compound with two OH groups (61) has much less.

In summary, all the above observations support the following mechanism for chemical etching of the *α*-SiC:H overcoat film under operating conditions relevant to thermal ink jet: (1) The thin SiO_x surface layer is dissolved in the test solution, which process may be accelerated by the presence of, say, OH anion or radical; (2) the dissolved silicon and carbon species (silicates, CO, CO_2, etc.) are readily removed from the surface region by the vigorous, recurring motion associated with bubble growth and collapse, exposing a fresh *α*-SiC:H surface; (3) the surface is reoxidized at high temperatures. Thus, the unique mechanism of effective removal of reaction products contributes to both a thin surface oxide and a linear etch rate.

Kogation. Kogation has been examined by several methods to determine its composition, and all the data indicate that it is mostly carbon, with lesser amounts of other elements; the data for an Auger analysis of heaters exposed to a representative test fluid are contained in Table III. These values are typical, although at times 5–10% Si has been observed, which is probably due to etching of the sample and mixing of this generated SiO_x with the kogation.

Mechanism of kogation: As noted in the Introduction, there are studies that attempt a few correlations with kogation.[7] Most of the kogation processes, and there probably are several due to the many variations in the nature of the kogation we observe, are not well understood. We have seen optically transparent kogation, kogation not removed by the most vigorous rubbing or scraping of the heater surface, flake-type kogation, sintered looking kogation, very friable kogation that is easily wiped off by the slightest pressure, and kogation that changed its nature with a change in pH.

Kogation correlates directly with increasing carbon content; in many cases, an increase in the number of carbon atoms in a molecule results in an increase in kogation. The simultaneous occurrence of kogation and etching complicates matters. We have observed etching under kogation and etching down to substrate next to places with very severe kogation on the same heater. In short, the relation between kogation and etching is not known, and the correlation of structure with kogation is likewise not completely known, with only a few empirical effects as noted above. If a change is made in a molecule that previously etched but did not kogate and the new molecule does not etch but kogates, it is easy to rationalize this as due to the balance between the two: the etching of the new molecule is subdued because of the increase in kogation rate. One possibility is that the decrease in etch rate occurs simply because the etching species occupied nibbling at the renewed kogation deposits and never reach the heater. Perhaps practical inks and their components merely achieve the correct balance between kogation and etching, and both phenomena operate continuously.

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(23) Washburn, W. N.; et al. *J. Am. Chem. Soc.* **1978**, *100*, 5863–74.
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If, as our results suggest, kogation and etching are properties of functional groups, polyfunctional molecules may do both, and the resultant effect could be very subtly balanced.

Given the composition of kogation as some sort of reduced form of carbon, possibly polymeric, the kogation processes might take any one of the forms described as follows, and all may operate independently: (1) Kogation is produced by a radical polymerization process at high temperatures. (2) Kogation is produced by a base-catalyzed polymerization at high temperatures. (3) Kogation is produced by decomposition at elevated temperatures that is predominantly anaerobic.

Conclusions

Kogation and etching in thermal ink jet devices are derived from the thermal activation of ink ingredients. Etching can arise from high pH, radicals, or both. Kogation can arise from chemicals with a preponderance of carbon. Relatively low amount (ca. 0.1%) of an offensive component can produce poor performance. The fraction of the offensive chemical that decomposes to either etch or kogate is probably small, on the order of 0.01%. The interaction of etching and kogation is complicated and can give rise to all possible combinations: net etching, net kogation, or no adverse behavior.

Mechanism of Nucleation and Atomic Layer Growth of AlN on Si

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We have studied by X-ray photoelectron spectroscopy the adsorption and decomposition of trimethylaluminum (TMA) on Si(100), the low-temperature formation of AlN from pyrolysis of TMA and NH$_3$, and have demonstrated a mechanism for atomic layer growth of AlN at 600 K. TMA adsorbs dissociatively to Si at temperatures above 300 K. At <650 K adsorption is self-limiting at <1 monolayer, with most carbon remaining in the form of CH$_3$. At higher temperatures, decomposition of the TMA is rapid, and continuous deposition is observed with production of carbides as the primary product. Coadsorption of TMA and NH$_3$ at room temperature leads to formation of Al–N covalent bonding as well as a surface adduct species, Al:N, which is converted quantitatively to Al–N at higher temperature. At substrate temperatures <550 K, coadsorption of TMA and NH$_3$ is self-limiting at less than a monolayer, while above this temperature reaction to form AlN is rapid and continuous deposition is observed. Self-limiting adsorption of TMA at <650 K and rapid, site-selective reaction with NH$_3$ to form AlN at >550 K satisfy the conditions for atomic layer growth of AlN at 600 K using sequential exposures of TMA and NH$_3$. The chemical nature of the interfacial and growth surface are discussed.

Introduction

We have undertaken extensive studies of the low-temperature chemical vapor deposition (CVD) of AlN[1,2] because of the many potential applications of this material in microelectronic and sensor technologies and as a model system for the study of low-temperature preparation of ceramic thin films in general. CVD offers many advantages in terms of process flexibility and control of material properties but demands a great deal of understanding of the mechanisms and kinetics of film growth to realize these advantages.

To this end, we previously investigated the adsorption and decomposition of trimethylaluminum (TMA) on SiO$_2$[1] and the initial stages of AlN formation from TMA and NH$_3$ on SiO$_2$.[2] In these studies we demonstrated the dissociative chemisorption of TMA on this substrate and the transformations of the organic ligands over the temperature range of interest to CVD processes. We inferred from infrared spectroscopic evidence that adsorbed alkylaluminum species form a Lewis acid–base adduct with NH$_3$ which may serve as a precursor to formation of an

Al–N covalently bonded network at temperatures <600 K. We have also proposed that elimination of methane from the surface can occur via inter- and intraadsorbate reactions between methyl groups from the alkylaluminum species and H from the NH$_3$. Recently Yu et al.[3] demonstrated preparation of high-quality AlN at low temperature by surface reaction of TMA and NH$_3$ on Si and Al$_2$O$_3$ substrates.

Here we conduct similar studies of initial stages of AlN growth from TMA and NH$_3$ on Si, in part to complement the infrared studies, as well as to demonstrate the control of film growth that can be achieved by controlling the surface chemistry. In this case we have demonstrated a mechanism for atomic layer growth of AlN.

Atomic layer growth of III–V semiconductor materials by chemical vapor deposition techniques has been demonstrated by a number of laboratories.[4–9] This process

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(3) Yu, Z. J.; Edgar, J. H.; Ahmed, A. U.; Rys, A. *J. Electrochem. Soc.* 1991, *138*, 196.
(4) Nishizawa, J.; Abe, H.; Kurabayashi, T. *J. Electrochem. Soc.* 1985, *132*, 1197.