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Synthesis of Pure Tetramethylammonium Hydroxide Solution Free from Chloride Ion by the Electrolysis of Its Hydrogen Carbonate

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Tetramethylammonium hydroxide solution free from chloride ion was produced by the electrolysis of tetramethylammonium hydrogen carbonate using a cation exchange membrane as a diaphram. The hydrogen carbonate was prepared by the reaction of trimethylamine and dimethyl carbonate in methanol.

In the manufacturing process of IC and LSI devices, chemicals are important in washing the surface of a silicon wafer and in the developement of a resist film. Particulaly tetramethylammonium hydroxide (TMAH) 1, which is free from inorganic ions, is important as an organic base.1)

TMAH 1 has been synthesized by the electrolysis of the halide salt of quarternary ammonium ion 2 using a cation-exchange membrane as a diaphragm (Eq. 1). The ammonium halide is prepared from trimethylamine 3 and methyl chloride 4 in methanol (Eq. 2).2) In this method, the cation-exchange membrane does not inhibit completely the permeation of chlorine and chloride ion into a catholyte (TMAH solution). The TMAH solution thus obtained induces corrosion of the aluminium interconnection which formed on semiconductor substrates. This phenomena cause a serious deterioration in semiconductor devices.

$$\underset{\underline{2}}{(CH_3)_4N^+Cl^-} + H_2O \xrightarrow{e^-} \underset{\underline{1}}{(CH_3)_4N^+OH^-} + 1/2\ Cl_2 + 1/2\ H_2 \qquad (1)$$

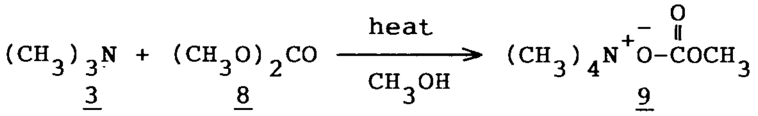
$$\underset{\underline{3}}{(CH_3)_3N} + \underset{\underline{4}}{CH_3Cl} \xrightarrow[CH_3OH]{} \underset{\underline{2}}{(CH_3)_4N^+Cl^-} \qquad (2)$$

We reported the preparation of a chloride free TMAH solution by using methyl formate 5 instead of methyl chloride 4 and electrolysis of the resulting formate 6 (Eqs. 3 and 4).3) It was reported that formic acid generated by the electrolysis is further electrolyzed to carbon dioxide by using a Pt electrode in acidic media.[4)] However, small amount of formic acid persists and moves into the catholyte in this process.

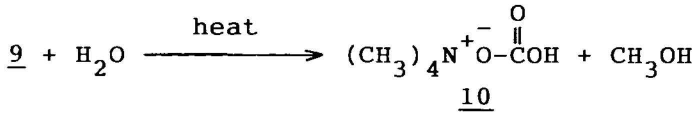
$$\underset{\underline{3}}{(CH_3)_3N} + \underset{\underline{5}}{HCOOCH_3} \xrightarrow[CH_3OH]{heat} \underset{\underline{6}}{(CH_3)_4N^+HCOO^-} \qquad (3)$$

$$\underline{6} + H_2O \xrightarrow{e^-} \underset{\underline{1}}{(CH_3)_4N^+OH^-} + \underset{\underline{7}}{1/2\ HCOOH} + 1/2\ CO_2 + 1/2\ H_2 \qquad (4)$$

In this paper we like to report the preparation of TMAH solution free from chloride ion and formic acid by using dimethyl carbonate $\underline{8}$ as an starting material (Eqs. 5, 6, and 7).



$$\underset{\underline{3}}{(CH_3)_3N} + \underset{\underline{8}}{(CH_3O)_2CO} \xrightarrow[CH_3OH]{heat} \underset{\underline{9}}{(CH_3)_4N^+\,{}^-O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}OCH_3} \qquad (5)$$



$$\underline{9} + H_2O \xrightarrow{heat} \underset{\underline{10}}{(CH_3)_4N^+\,{}^-O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}OH} + CH_3OH \qquad (6)$$

$$\underline{10} + H_2O \xrightarrow{e^-} \underset{\underline{1}}{(CH_3)_4N^+OH^-} + CO_2 + 1/2\ H_2 + 1/4\ O_2 + 1/2\ H_2O \qquad (7)$$

Tetramethylammonium carbonate $\underline{9}$ was prepared by the reaction of trimethylamine $\underline{3}$ and dimethyl carbonate $\underline{8}$ in methanol by using a stainless steel autoclave (1500 ml). To seek the best conditions for the reaction, we tested the reagents ratio, temperature, and the reaction time. The results are summarized in Table 1.

Table 1. Reaction of trimethylamine $\underline{3}$ and dimethyl carbonate $\underline{8}$ under various conditions[a)]

Run	$\underline{3}$/g	$\underline{8}$/g	[$\underline{3}$]/[$\underline{8}$]	Temp/°C	Time/h	$\underline{9}$/g	Yield from $\underline{3}$/%[b)]
1	208	159	2.0	165	5.5	235	43.7
2	208	159	2.0	144	5.5	251	47.7
3	104	159	1.0	113	5.5	250	91.2
4	104	159	1.0	78	7.5	170	64.4

a) 200 g of methanol was used as solvent.

b) Tetramethylammonium ion was measured by HCl titration.

The results show that trimethylamine 3 and dimethyl carbonate 8 react in an equivalent molecular ratio and one of the two methoxy group was incorporated into 9. The solution of hydrogen carbonate 10 5), free from methanol, was placed in the electrolytic chamber of polypropylene with a cation-exchange membrane (du Pont, Nafion 324 6)) as a diaghragm. The chamber equipped with a Ti-plate anode coated by IrO_2 and a cathode of stainless steel (SUS 304).

The relation between TMAH formation and consumed chagre is shown in Fig. 1. Linear relation between the formation of TMAH and the consumed charge indicates the high efficiency and the lack of side reaction. The ammonium hydrogen cabonate 10 was electrolyzed with a high efficiency and 93.3% of the ammonium ion migrated into the catholyte under the present conditions. The current efficiency was 84.6% and the concentration of carbon dioxide contaminated in this 30.7% TMAH solution was lower than 10 ppm. 7)

The TMAH solution prepared by the present procedure contained much less ammount of metallic ions (< 10 ppb) (Table 2) than TMAH by other methods.

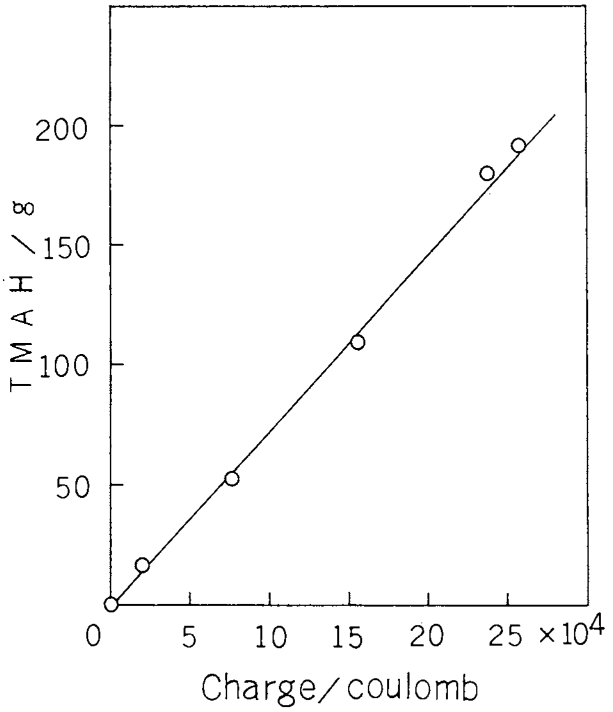


Fig. 1. TMAH formation and the consumed charge (20 V,12 h).

The new process described in this paper offers an improved preparation and usefulness of TMAH in semiconductor industries.

Table 2. Analytical results of impurities in 30.7% TMAH solution a)

Element	Na	Ca	Al	Fe	Cr	Ni	Mg	Mn	Zn	Cu
Content (ppb)	5	2	2	4	< 1	< 1	< 1	< 1	< 1	< 1

a) Detected by graphite furnace atomic absorption spectrometry.

Practical Procedure: Tetramethylammonium methylcarbonate solution prepared as mentioned above was evaporated under vacuum to dryness to get a white crystalline carbonate 9. The carbonate 9 thus obtained was dissolved in purified water and heated to hydrolyze and remove the resultant methanol (Eq. 6). The 63.0% solution (482 g) of 10 (2.25 mol) in 120 ml of purified water was reserved in a 1000 ml polyethylene bottle and was circulated through the anodic chamber. In the same manner, 240 g of purified water containing small amount of TMAH 1 as an electrolyte was circulated through the cathodic chamber. Electrolysis was performed by applying 20 V for 12 h to give 626 g of 30.7% TMAH solution.

References

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5) 10: ^{13}C NMR (D_2O) 57.6 ppm-CH_3 (3.9) and 162.7 ppm-HCO_3 (1.0).
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7) The concentration of carbone dioxide was measured by an Ion Meter; Model IM-5S, Toa Denpa Kogyo, Tokyo.

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