

A Method For Purification Of Acids For Use In Semiconductor Processing

Background of this Invention

Various acids and their derivatives are used as chelating agents for removal of cationic impurities in the manufacture of semiconductors and must be provided to these manufacturers in increasingly purer forms to keep up with the ever smaller dimensions of the integrated circuits. These acids include carboxylic acids having at least two carboxylic acid groups, and include C₂ to C₆ dicarboxylic acids, hydroxycarboxylic acids and aminocarboxylic acids. Specific examples of C₂ to C₆ acids includes oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid. Examples of hydroxy carboxylic acids includes malic acid, tartaric acid and citric acid. Examples of aminocarboxylic acids include ethylenediaminetetracetic acid (EDTA) and hydroxyethylenediaminetriacetic acid (HEDTA). A preferred acid is citric acid. A preferred derivative is ammonium citrate.

Typically, the acids are well known, for instance malonic acid is used as an intermediate for barbiturates and pharmaceuticals. Oxalic acid is also used for automobile radiator cleaners, general metal and equipment cleaning, as a purifying agent and intermediate, for leather tanning, as a catalyst, as a laboratory reagent, as a stripping agent for permanent press resins, for textile bleaching and in rare earth processing. Citric acid is known as an effective ingredient in the cleaning industry and is typically used in bathtub and faucet cleaners, liquid laundry detergent, and oven cleaners. In the steel industry, citric acid solutions are known to remove corrosion and oxides from steel equipment. Although citric acid is used to a limited extent in the semiconductor industry, commercially available citric acid is not of the desired quality.

Commercially available food grade citric acid has been purified by a strong acid cation ion exchange resin. The resultant citric acid is superior to previously available food grade citric acid.

Citric acid is made commercially by the fermentation of molasses. Ion
5 exchange resins have been used to recover citric acid after fermentation(EP 324210) as well as remove sulfates and chlorides from citric acid solutions using anion exchange(Pishch. Prom-st (Moscow)(1988),(11),30-2). Cation and anion ion exchange membranes have been used to separate citric acid from saccharides and proteins(JP 43024887) but do not produce the high purity citric acid required by the
10 semiconductor manufacturers.

Today, the current industrial grades of citric acid and ammonium citrate contain cationic impurities which include iron, calcium, and barium at levels that are not favorable to semiconductor processing. This invention provides, in general, purified carboxylic acids and their derivatives and in particular purified citric acid,
15 malonic acid, oxalic acid and ammonium citrate useful to integrated circuit manufacturers.

The semiconductor industry needs ultra high purity chelating agents such as citric acid, malonic acid, oxalic acid and ammonium citrate. By using a strong acid ion exchange resin such as a styrene-divinylbenzene cross linked resin with sulfuric acid or
20 hydrochloric functionality, metal impurities in solutions of acids can be removed. Ammonium citrate can be made by reacting purified citric acid with high purity ammonium hydroxide.

Post-Chemical Mechanical Polishing (CMP) uses a citrate, which is a cleaning agent and is described in POST-CMP cleaning of Wand SiO₂: "A Model Study", Mat. Res. Soc. Symp. Proc. Vol. 386, 1995 Materials Research Society. Malik pages 109-114.

5 **Brief Summary of the Invention**

One aspect of this invention is a highly purified citric acid composition for use in cleaning after chemical mechanical polishing of integrated circuits. Chemical mechanical polishing is described in PCT/US96/00156 to Advanced Micro Devices, U.S. Serial No. 08/391,812. Citric acid compositions of the present invention have
10 less than 100 ppb iron cations, 20 ppb calcium cations, and 100 ppb barium cations, preferably less than 10 ppb for a cationic impurity. The citric acid of the present invention is prepared by exposing technical grade citric acid in deionized water to a styrene-divinyl benzene cation exchange resin having sulfonic acid or hydrochloric acid functionality and collecting said ion exchanged effluent. In another aspect this
15 invention provides a method of cleaning wafers after chemical mechanical polishing comprising exposing the surface of said wafers to a purified citric or ammonium citrate solution having less than 100 ppb Fe⁺, 20 ppb Ca⁺⁺ and 10 ppb Ba⁺, preferably less than 10 ppb for each of the cationic impurities.

The following examples use metric system units. All patents mentioned herein
20 are specifically incorporated by reference.

Example 1

Industrial grade citric acid was dissolved in water to make a 28.8% solution.

This solution was passed through Amberlyst 35 ion exchange column at 2 BV/hr (BV is Bed Value). The starting material (See Table below -5874-56-1) has high levels of calcium, iron, sodium, and other metallic contamination. After purification, the

5 metallic impurities, detrimental to semiconductor processing, have been substantially removed (See Table below - 5874-56-3). The citric acid was converted to ammonium citrate by neutralization with high purity ammonium hydroxide.

Example 2

10 ADM USP grade citric acid, anhydrous fine granular was dissolved in ultrapure DI water. This solution was purified in a 3" diameter column with ion exchange resin. The starting material is so high in calcium as to saturate the detector(see table below - 5874-76 Starting Material). After purification, the citric acid has a calcium level of 26 ppb(See table below 5874-76 Purified).

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Example 3

A procedure similar to Example 2 was used to purify citric acid. Results show that after citric acid solution is contacted with Amberlyst 35, the citric acid is suitable for use in semiconductor applications(See table below 5874-76-1(starting material) and
20 purified material(5874-76-3)).

Example 4

A procedure similar to Example 2 was used to purify citric acid except the flow rate through the column was 4 BV/Hr. The calcium level in the industrial grade of citric acid solution was 5.6 ppm. After contacted with Amberlyst 35, the calcium level in citric acid had been reduced to 47 ppb. This level is suitable for use in

5 semiconductor applications.

EXAMPLE 1		Citric Acid	Citric Acid
Element		#5874-56-1	#5874-56-3
Al		72	<10
Sb		<10	<10
As		<10	<10
Ba		278	<10
Be		<10	<10
Bi		<10	<10
B		<10	<10
Ca		>1000 **	18
Cr		327	<10
Co		<10	<10
Cu		24	39
Ga		<10	<10
Ge		<10	<10
Fe		553	15
Pb		<10	11
Li		<10	<10
Mg		14	<10
Mn		<10	<10
Mo		<10	<10
Ni		59	<10
Nb		<10	<10
K		89	<10
Se		<10	<10
Si		<10	<10
Ag		<10	<10
Na		329	<10
Sr		19	<10
Ta		<10	<10
Tl		<10	<10
Sn		<10	<10
Ti		<10	<10
W		<10	<10
V		<10	<10
Zn		74	15
Zr		<10	<10

EXAMPLE 2	Citric Acid	Citric Acid		EXAMPLE 3	Citric Acid	Citric Acid
	5874-76	5874-76				
Element	Purified	Batch #2			#5874-76-1	#5874-76-3
		Starting Material				
Al	48	170			151	17
Sb	<10	<10			<10	<10
As	<10	<10			<10	<10
Ba	<10	251			>1000 **	<10
Be	<10	<10			<10	<10
Bi	<10	<10			<10	<10
B	<10	<10			11	<10
Ca	26	>1000 **			>1000 **	28
Cd	<10	<10			<10	<10
Cr	23	42			17	<10
Co	<10	<10			<10	<10
Cu	38	<10			68	89
Ga	<10	<10			<10	<10
Ge	<10	<10			<10	<10
Au	<10	<10			<10	<10
Fe	616	646			106	16
Pb	<10	<10			<10	<10
Li	<10	<10			<10	<10
Mg	<10	<10			34	<10
Mn	<10	<10			<10	<10
Mo	<10	<10			<10	<10
Ni	18	<10			59	<10
Nb	<10	<10			<10	<10
K	100	79			142	79
Se	<10	<10			<10	<10
Si	90	<10			229	<10
Ag	<10	<10			<10	<10
Na	62	23			691	23
Sr	<10	<10			52	<10
Ta	<10	<10			<10	<10
Tl	<10	<10			<10	<10
Sn	<10	<10			<10	<10
Ti	<10	<10			<10	<10
W	<10	<10			<10	<10
V	<10	<10			<10	<10
Zn	92	10			<10	10
Zr	<10	<10			<10	<10
* All results expressed in parts per billion .						
** Results saturated the detector .						

Example 5

Industrial grade oxalic acid was treated with Amberlyst 35 ion exchange resin as described in Examples 1 and 2. The analysis is reported in the following table.

Element	Oxalic Acid 5874-97-1	Oxalic Acid 5874-97-2
	Starting Material	
Al	71	24
Sb	<5	<5
As	<5	<5
Ba	9	<5
Be	<5	<5
Bi	<5	<5
B	<5	<5
Ca	>1000 **	38
Cd	<5	<5
Cr	16	6
Co	<5	<5
Cu	6	5
Ga	<5	<5
Ge	<10	<10
Au	<5	<5
Fe	127	42
Pb	5	<5
Li	<5	<5
Mg	269	<5
Mn	21	<5
Mo	5	<5
Ni	59	<5
Nb	<5	<5
K	666	253
Se	<5	<5
Si	24	<5
Ag	<5	<5
Na	1891	12
Sr	5	<5
Ta	<5	<5
Tl	<10	<10
Sn	<5	<5
Ti	<5	<5
W	<5	<5
V	22	15
Zn	17	<5
Zr	<5	<5

*All results expressed in parts per billion.

**Results saturated the detector.

Example 6

A procedure similar to Example 1 was used to purify citric acid except that the solution was passed through an Amberlyst 15 containing ion exchange column. After purification, impurities detrimental to semiconductor processing have been

5 substantially removed.

	28% Citric Acid
Aluminum	<10
Barium	<10
Calcium	<10
Chromium	<10
Copper	<10
Iron	<10
Magnesium	<10
Manganese	<10
Nickel	<10
Potassium	2200
Silicon	<10
Sodium	<10
Titanium	<10
Zinc	<10

All results are reported in ppb unless otherwise noted.



I claim

1. A method for the purification of an acid useful as a chelating agent in semiconductor manufacturing, comprising the step of passing an aqueous solution of said acid through at least one ion exchange resin bed which has been treated with strong acid.
2. The method of claim 1 where said strong acid is sulfuric acid or hydrochloric acid.
3. The method of claim 1 where said resin is a styrene-divinylbenzene crosslinked resin.
4. The method of claim 1 where said resin has sulphonic acid functionality.
5. The method of claim 1, where the acid is a carboxylic acid having at least two carboxylic acid groups selected from the group consisting of C_2 to C_6 dicarboxylic acids, hydrocarboxylic acids and aminocarboxylic acids.
6. The method of claim 1, comprising an aqueous solution of citric acid.
7. The method of claim 1, comprising an aqueous solution of oxalic acid.
8. The method of claim 1, wherein said purified acid contains less than 100 parts per billion iron cations, less than 20 parts per billion calcium cations, and less than 100 parts per billion barium cations.
9. A purified acid composition prepared by the process of Claim 1.
10. A method of making high purity ammonium citrate useful in the manufacture of integrated circuits, comprising the steps of;

passing citric acid through at least one strong acid ion exchange resin bed which has been treated with strong acid,

collecting said ion-exchanged acid,

adding high purity ammonium hydroxide, and

forming high purity ammonium citrate.
11. The method of claim 10 wherein said strong acid is sulfuric acid or hydrochloric acid.



12. The method of claim 10 wherein said resin is a styrene-divinylbenzene crosslinked resin.
13. The method of claim 10 wherein said resin has sulphonic acid functionality.
14. The method of claim 10 wherein said purified ammonium citrate contains less than 100 parts per billion iron cations, less than 20 parts per billion calcium cations, and less than 100 parts per billion barium cations.
15. Purified ammonium citrate prepared by the method of claim 10.