

TREATMENT OF ORGANIC CONTAINING WASTEWATER USING MODIFIED
FENTON'S REAGENT

FIELD OF TECHNOLOGY

Aspects and embodiments disclosed herein relate to systems and methods for the
5 treatment of wastewater, for example, copper chemical-mechanical polishing (CMP)
wastewater including organic contaminants such as azoles. The methods disclosed herein
provide for the destruction of organic contaminants in the wastewater utilizing a modified
Fenton's reagent.

10 SUMMARY

In accordance with one aspect, there is provided a method for removing one or more
azoles from wastewater of a semiconductor production facility. The method comprises
obtaining copper from the wastewater and introducing an oxidizer into the wastewater to
produce hydroxyl radicals from the oxidizer to react with the one or more azoles, wherein the
15 copper catalyzes the production of the hydroxyl radicals from the oxidizer.

In some embodiments, the method further comprises maintaining a pH of the
wastewater at a level at which the copper catalyzes the production of the hydroxyl radicals
from the oxidizer.

In some embodiments, the method further comprises obtaining the wastewater from a
20 copper chemical mechanical polishing (CMP) operation of the semiconductor manufacturing
facility.

In some embodiments, removing the one or more azoles from the wastewater includes
removing one or more of 1,2,4-triazole, pyrazole, Benzotriazole, 5-methyl 1H-benzotriazole
(Tolutriazole), or 3-amino 1,2,4-triazole from the wastewater.

25 In some embodiments, introducing the oxidizer into the wastewater includes
introducing hydrogen peroxide into the wastewater.

In some embodiments, the method further comprises obtaining the hydrogen peroxide
from a waste stream from the semiconductor manufacturing facility.

In some embodiments, the copper is present in the wastewater in the form of copper
30 sulfate.

In accordance with another aspect, there is provided a system for removing one or
more azoles from copper-containing wastewater from a semiconductor manufacturing
facility. The system comprises a vessel fluidly connectable to a source of the wastewater, a

source of oxidizer configured to introduce the oxidizer into the wastewater in the vessel, the copper catalyzing production of hydroxyl radicals from the oxidizer to react with the one or more azoles, and a source of pH adjustment chemical configured to introduce the pH adjustment chemical into the wastewater in the vessel.

5 In some embodiments, the system further comprises a pH monitor disposed within the vessel, and a controller configured to control the source of pH adjustment chemical to introduce the pH adjustment chemical into the wastewater in the vessel at a quantity and rate sufficient to maintain the pH of the wastewater at a level at which the copper catalyzes production of hydroxyl radicals from the oxidizer.

10 In some embodiments, the wastewater includes one or more of 1,2,4-triazole, pyrazole, Benzotriazole, 5-methyl 1H-benzotriazole (Tolutriazole), or 3-amino 1,2,4-triazole and the system is configured to decompose the one or more of 1,2,4-triazole, pyrazole, Benzotriazole, Tolutriazole, or 3-amino 1,2,4-triazole with the hydroxyl radicals.

15 In some embodiments, the wastewater is a copper chemical mechanical polishing (CMP) wastewater at the semiconductor manufacturing facility.

 In some embodiments, the copper is in the form of copper sulfate.

 In some embodiments, the source of oxidizer is a source of hydrogen peroxide.

 In some embodiments, the source of hydrogen peroxide includes a waste stream of the semiconductor manufacturing facility.

20

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing is not intended to be drawn to scale. In the drawing, each identical or nearly identical component that is illustrated is represented by a like numeral.

For purposes of clarity, not every component may be labeled. In the drawings:

25 FIG. 1 illustrates an example of a system as disclosed herein.

DETAILED DESCRIPTION

30 The chemical mechanical polishing (CMP) planarization process involves a polishing slurry comprising an oxidant, and abrasive, complexing agents, and additional additives to remove and/or etch semiconducting wafers during the manufacturing process. The polishing is performed with a polishing pad to remove excess copper from the semiconductor wafers. Silicon, copper, and various trace metals are removed from the silicon structure via the polishing slurry. The polishing slurry is introduced to the silicon wafer on a planarization table in conjunction with polishing pads. Oxidizing agents and etching solutions are

introduced to control the removal of material. Deionized water rinses are generally employed to remove debris from the silicon wafer. UPW from reverse osmosis (RO), demineralized, and polished water may also be used in the semiconductor fabrication facility tools to rinse the silicon wafer.

5 An oxidizer of hydrogen peroxide (H_2O_2) typically is used to help dissolve the copper from the microchip. Accordingly, hydrogen peroxide (H_2O_2) at a level of about 300 ppm and higher also can be present in the byproduct polishing slurry wastewater.

 In fabrication processes of semiconductor devices, large amounts of wastewater containing anticorrosives for copper are discharged from CMP steps for performing surface
10 polishing of copper when copper wiring is installed. Therefore, treatment of the wastewater is desirable to prevent discharge of undesirable contaminants to the environment.

 Among anticorrosives for copper, in particular, azole-type anticorrosives for copper have an excellent anticorrosive effect. However, the azole-type anticorrosives for copper typically have a chemically stable structure and are not easily biodegraded. Thus,
15 conventionally, in treating wastewater containing an azole-type anticorrosive for copper discharged from the process, the azole-type anticorrosive for copper is decomposed using an oxidizing agent having high oxidizing power, such as ozone, ultraviolet light, or hydrogen peroxide, or by an advanced oxidation process in which these oxidizing agents are combined, and then treated water is discharged or collected.

20 However, as described above, since the azole-type anticorrosives for copper are chemically stable, even when using of an oxidizing agent having high oxidizing power, such as ozone, addition of a large amount thereof is required for oxidative decomposition of the azole-type anticorrosives for copper, thus posing a large problem in terms of cost. In particular, in recent years, with the increase in the degree of integration in semiconductor
25 devices, the number of fine polishing steps has been increasing, and along with this, the amount of polishing wastewater discharged has been increasing. Therefore, the increase in cost due to an increase in the capacity of wastewater treatment equipment has become a problem.

 Fenton's reagent is often used for the treatment of organic compounds. Fenton's
30 reagent may be produced by adding 10 parts of peroxide to 1 part of ferrous iron (ferrous sulfate) for every 0.3 parts of organic compounds. Fenton's reagent is effective when treating some azoles, such as pyrazole. However, lab tests have showed that other forms of azoles such as 1,2,4-Triazole are not decomposed when exposed to Fenton's reagent.

As discussed above, azoles are often used in facilities that manufacture computer chips as an anticorrosive additive. These facilities also generally have high strength copper bearing wastewaters from the CMP process that, once spent, are treated and disposed of at a cost to the facility. In one embodiment, the use of a waste copper stream in place of iron in Fenton's reagent is used to treat and degrade azole compounds in wastewater. Testing has shown that 1,2,4-Triazole, 1H-Benzotriazole, and Methylbenzotriazole: 4,5 Tolytriazole can all be treated using copper-substituted Fenton's reagent. In one test waste hydrogen peroxide (which contained the azole to be treated), and waste copper sulfate, which can be used in place of iron sulfate in the Fenton's reaction was found to produce an oxidant containing solution which successfully degraded the azole.

In some embodiments, copper is substituted for iron in a modified Fenton's reaction, referred to herein as a Fenton's-like reaction. A waste copper stream from a semiconductor production facility plant may be used as the source of the copper. The waste copper may be present in the effluent of a copper CMP process.

As noted above, the wastewater from semiconductor production facilities or other industrial sources may include high levels of azoles, for example, from about 20 mg/l up to about 200 mg/l total azoles or greater, that are used as anticorrosive agents for copper during the wafer planarization and polishing process. The wastewater from these processes may also include heavy metals, additional organic compounds, for example, alcohols, and/or surfactants such as ammonium salts, and inorganic abrasives, such as colloidal silica, all of which should be removed prior to discharge of the wastewater. These additional contaminants may be present at levels from about 0.01 wt% up to about 1 wt%. The wastewater may further have a high background total organic carbon (TOC) concentration, with the total azoles comprising a portion of the TOC. For example, oxidizers such as hydrogen peroxide (H₂O₂) are generally used to assist in dissolving copper from microchips and may be present in CMP wastewater at concentrations exceeding 1,000 mg/L or 0.1 wt%.

Azoles are not currently regulated for maximum contaminant levels (MCL) by regulatory authorities in the United States but are believed to have a negative impact on the environment upon discharge into open waterways. Recent evidence has indicated bioaccumulation of azoles in fish and incidences of toxicity of naturally occurring algae blooms, necessitating their removal from process water before discharge.

As described in US Patent No. 8,801,937, the disclosure of which is herein incorporated by reference in its entirety for all purposes, azole compounds are widely used in the semiconductor industry as anticorrosive agents for copper during silicon wafer

processing. Examples of such azole compounds include, but are not limited to, imidazole, pyrazole, oxazole, isoxazole, thiazole, isothiazole, selenazole, 1,2,3-triazole, 1,2,4-triazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,3,4-thiadiazole, tetrazole, 1,2,3,4-thiatriazole, any derivatives thereof, amine salts thereof, and metal salts thereof. Examples of azole derivatives include compounds having a fused ring of an azole ring and a benzene ring or the like, such as indazole, benzimidazole, benzotriazole, and benzothiazole, and further include derivatives thereof, such as alkylbenzotriazoles (e.g., benzotriazole, *o*-tolyltriazole, *m*-tolyltriazole, *p*-tolyltriazole, 5-ethylbenzotriazole, 5-*n*-propylbenzotriazole, 5-isobutylbenzotriazole, and 4-methylbenzotriazole), alkoxybenzotriazoles (e.g., 5-methoxybenzotriazole), alkylaminobenzotriazoles, alkylaminosulfonylbenzotriazoles, mercaptobenzotriazoles, hydroxybenzotriazoles, nitrobenzotriazoles (e.g., 4-nitrobenzotriazole), halobenzotriazoles (e.g., 5-chlorobenzotriazole), hydroxyalkylbenzotriazoles, hydrobenzotriazoles, aminobenzotriazoles, (substituted aminomethyl)-tolyltriazole, carboxybenzotriazole, N-alkylbenzotriazoles, bisbenzotriazole, naphthotriazole, mercaptobenzothiazoles, aminobenzothiazole, amine salts thereof, and metal salts thereof.

One embodiment of a system for treating azole-containing wastewater from a semiconductor production facility is shown schematically in FIG. 1. A semiconductor production facility 110 typically includes hundreds of unit operations, three of which are identified in FIG. 1. The unit operations identified in FIG. 1 are a copper CMP unit operation 120, a unit operation 130 that produces wastewater with a high concentration of dissolved copper, for example, a copper plating operation, and a unit operation 140 that produces wastewater having a high concentration of hydrogen peroxide, for example, one of the wafer cleaning unit operations within the semiconductor manufacturing facility 110. The disclosed system is utilized to decompose organic contaminants such as azoles present in wastewater from the copper CMP unit operation 120 utilizing a Fenton's-like reaction in which copper is utilized to catalyze the production of hydroxyl radicals from hydrogen peroxide. The hydroxyl radicals decompose the organic contaminants by oxidation into less objectional byproducts such as nitrogen oxides (NO₂/NO₃), carbon dioxide, and water.

Wastewater from the CMP unit operation 120 is directed into a vessel 150, for example, by a pump P1. An oxidizer, for example, hydrogen peroxide from a source of oxidizer 160 is added to the wastewater in the vessel 150, for example, using another pump P4 in an amount and at a rate sufficient to maintain a concentration of hydrogen peroxide in the vessel at a desired level, for example, 300 mg/L or greater, to facilitate reactions resulting

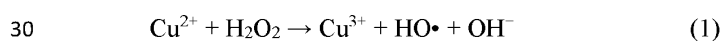
in decomposition of organic compounds in the wastewater. In some embodiments, addition of oxidizer from the source of oxidizer 160 may be supplemented by addition of hydrogen peroxide-containing wastewater from the unit operation 140, for example, using pump P3. If the hydrogen peroxide-containing wastewater from the unit operation 140 includes sufficient hydrogen peroxide, it may be utilized as the sole source of hydrogen peroxide added to the wastewater in the vessel 150.

In other embodiments, a persulfate salt such as ammonium persulfate, potassium persulfate, and/or sodium persulfate, may be utilized as the oxidizer. Aspects and embodiments disclosed herein are not limited by the type of oxidant added in the treatment system. Peroxides produce hydroxyl and hydroperoxyl radicals and persulfates produce persulfate radicals when reacting with dissolved copper in the vessel 150.

A source of pH adjustment chemical 170, for example, a source of sulfuric acid and/or sodium hydroxide may add pH adjustment agent into the wastewater in the vessel 150 in an amount and at a rate sufficient to maintain the pH of the wastewater in the vessel at a desired level, for example, between 2 and 4 or about 3 to facilitate reactions resulting in decomposition of organic compounds in the wastewater.

The wastewater from the CMP unit operation 120 may include sufficient copper, for example, in the form of copper sulfate, to catalyze production of hydroxyl radicals from the hydrogen peroxide in the vessel 150 in a Fenton's-like reaction which will decompose one or more organic species in the wastewater in the vessel 150. Byproducts of the decomposition of the organic contaminants such as nitrogen oxides (NO_2/NO_3) and carbon dioxide may exit the vessel 150 through a vent V. The one or more organic species may include one or more azoles, for example, one or more of 1,2,4-Triazole, 1H-Benzotriazole, or Methylbenzotriazole; 4,5 Tolytriazole which may have been present in the wastewater from the CMP unit operation 120. The Fenton's-like reagent used for the decomposition of the azoles may be formed by adding about 500 mg/l to about 3,000 mg/l of an oxidant, such as hydrogen peroxide or a persulfate salt, to about 50 mg/l to about 300 mg/l of a soluble copper compound (e.g., copper (Cu^{2+}) sulfate).

The Fenton's-like reaction may occur in accordance with chemical equations (1)-(3):



The persulfate salt and the hydroxyl, hydroperoxyl, and persulfate radicals formed by the oxidation of Cu^{2+} or the reduction of Cu^{3+} may react with and decompose the azoles in the CMP wastewater into primarily nitrogen oxides (NO_2/NO_3), carbon dioxide, and water. Without wishing to be bound by any particular theory, the decomposition of a nitrogenous
5 organic molecule, such as an azole, may occur by the reaction illustrated in equation 4:



One or more sensors or monitors, for example, temperature, pH, ORP, chemical concentration sensors, etc., collectively indicated at “S” may be present in the vessel 150 in contact with the wastewater in the vessel. The one or more sensors S may be in
10 communication with a controller 190. The controller 190 may be a conventional computer including a conventional processor, for example, a Core® processor from the Intel Corporation and running a conventional operating system such as one of the versions of Windows® from the Microsoft Corporation and programmed to perform the functions disclosed herein. The controller may optionally be or include a specially programmed
15 controller such as an Application Specific Integrated Circuit (ASIC) programmed to perform the functions disclosed herein. The controller 190 is programmed or otherwise configured to control the source of pH adjustment chemical 170 to introduce the pH adjustment chemical into the wastewater in the vessel 150 at a quantity and rate sufficient to maintain the pH of the wastewater at a level at which the copper catalyzes production of hydroxyl radicals from
20 the oxidizer. The controller 190 may also control operation of any of the pumps P1-P6 to control, e.g., introduction of wastewater from the CMP unit operation 120, oxidizer from the source of oxidizer 160, hydrogen peroxide-containing wastewater from the unit operation 140, and removal of treated wastewater from the vessel 150.

In some embodiments, the wastewater from the CMP unit operation 120 may not
25 contain sufficient copper to catalyze production of sufficient hydroxyl radicals for decomposition of organic contaminants in the wastewater from the CMP unit operation 120 to levels that are as low as might be desired. Accordingly, additional copper may be added to the wastewater in the vessel 150 from, for example, the unit operation 130 that produces the wastewater with the high concentration of dissolved copper through a pump P2 operated by
30 the controller 190.

Wastewater from which organic compounds have been removed by decomposition by a Fentons’s-like reaction as disclosed herein in the vessel 150 may exit the vessel and be

directed, for example, by a pump P6 into a post-treatment system 180. The post-treatment system 180 may be used to remove residual copper and other undesired components from the partially treated wastewater exiting the vessel 150 using methods known in the art and may produce treated water that may be discharged to the environment, recycled, or sent for further treatment or disposal.

Aspects and embodiments disclosed herein are also directed to a method for removing one or more azoles from wastewater of a semiconductor production facility, for example, wastewater from a chemical mechanical polishing unit operation utilizing a Fenton's-like reagent. Removing the one or more azoles from the wastewater may include removing one or more of 1,2,4-Triazole, 1H-Benzotriazole, or Methylbenzotriazole: 4,5 Tolytriazole from the wastewater. The method may include obtaining copper from the wastewater. Wastewater from the chemical mechanical polishing unit operation may already include sufficient copper in the form of copper sulfate or another copper compound, so it may not be necessary to supplement the wastewater from the chemical mechanical polishing unit operation with additional copper. The method may further include introducing an oxidizer into the wastewater to produce hydroxyl radicals from the oxidizer to react with the one or more azoles, wherein the copper catalyzes the production of the hydroxyl radicals from the oxidizer. The pH of the wastewater may be maintained at a level at which the copper catalyzes the production of the hydroxyl radicals from the oxidizer. Introducing the oxidizer into the wastewater may include introducing hydrogen peroxide into the wastewater. In some embodiments, the hydrogen peroxide may be obtained from a waste stream from the semiconductor manufacturing facility.

Example

CMP slurry wastewater (Slurry Copper Waste - SCW) and wastewater having a high concentration of Cu (Concentrated Copper Waste – CCW), as well as a 25:1 mixture of the SCW and CCW from a semiconductor production facility was analyzed and found to include the contaminants listed in Table 1 below:

Table 1 – SCW and CCW Wastewater Analysis

Parameter	Units	Slurry Copper Waste (SCW)	Concentrated Copper Waste (CCW)	Blended Sample (25:1 SCW:CCW)
-----------	-------	---------------------------	---------------------------------	-------------------------------

Aluminum	mg/L	< 5.40	< 5.40	-
Ammonia	mg/LNH ₃ -N	56.5	< 0.35	41.9
Calcium	mg/L	0.02	4.00	-
Cobalt	mg/L	0.14	0.09	-
Copper	mg/L	20.0	22,000	Not analyzed
Magnesium	mg/L	0.03	0.98	-
Potassium	mg/L	42.0	< 2.20	-
Sodium	mg/L	0.37	12.0	-
Chloride	mg/L			-
Fluoride	mg/L			-
Nitrate	mg/L			-
Phosphate	mg/L			-
Sulfate	mg/L			-
1,2,4-Triazole	mg/L	32.8	-	33.1
Hydrogen Peroxide (H ₂ O ₂)	mg/L	< 8.0	1,210	41
pH	-	7.6	1.1	1.9
Total Kjeldahl Nitrogen (TKN)	mg/L			
Total Organic Carbon (TOC)	mg/L	130	67	106
Total Solids (TS)	mg/L		-	
Total Suspended Solids (TSS)	mg/L	25	-	44
Turbidity	NTU	23	5.8	52

Testing was performed to determine if the copper was present in the 25:1 mixture of the SCW and CCW in amount sufficient to catalyze production of sufficient hydroxyl radical to decompose the 1,2,4-Triazole present in the mixture. Details of the test conditions and results are presented in Table 2 below:

Table 2 – Azole decomposition using Fenton-like reaction in SCW:CCW mixture

	Unit	Blended 962 mL SCW and 38 mL CCW (25:1) at pH 3.0
Chemical Added Before Reaction		
NaOH	mg/L	1,142
Test Conditions		

Reaction Time	Mins	0	30	60	90	120
Temp.	°C	60	60	60	60	61
pH	-	3.0	3.0	3.0	3.0	3.0
Residual H ₂ O ₂	mg/L	0	522	743	596	400
H ₂ O ₂ Dose	mg/L	0	910	1,400	1,540	1,680
H ₂ SO ₄	mg/L	91	46	46	23	-
NaOH	mg/L	-	-	1,300	-	1,450
SBS ¹	mg/L	-	-	800	-	1,650
Test Results						
TOC	mg/L	106	-	24	-	11
TOC Removal	%	-	-	77%	-	90%
1,2,4-Triazole	mg/L	33.9	-	-	-	0.38
1,2,4-Triazole Removal	%	-	-	-	-	99%

¹ Sodium Bisulfate – decomposes H₂O₂

The pH of the blended sample (962 mL SCW + 38 mL CCW) was 3.0. A cumulative dose of 1,680 mg/L H₂O₂ over the 120-minute reaction time yielded 90% TOC removal and 0.38 mg/l azole residual (99% removal). These results were achieved without adding iron and show that copper already present in wastewater streams from a semiconductor production facility may be utilized as catalyst for a Fenton's-like reaction to successfully remove organic contaminants, including azoles, from those same wastewater streams.

The phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. As used herein, the term “plurality” refers to two or more items or components. The terms “comprising,” “including,” “carrying,” “having,” “containing,” and “involving,” whether in the written description or the claims and the like, are open-ended terms, i.e., to mean “including but not limited to.” Thus, the use of such

- terms is meant to encompass the items listed thereafter, and equivalents thereof, as well as additional items. Only the transitional phrases “consisting of” and “consisting essentially of,” are closed or semi-closed transitional phrases, respectively, with respect to the claims. Use of ordinal terms such as “first,” “second,” “third,” and the like in the claims to modify a claim
- 5 element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are performed, but are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

What is claimed is:

CLAIMS

1. A method for removing one or more azoles from wastewater of a semiconductor production facility, the method comprising:
 - 5 obtaining copper from the wastewater; and
 - introducing an oxidizer into the wastewater to produce hydroxyl radicals from the oxidizer to react with the one or more azoles, wherein the copper catalyzes the production of the hydroxyl radicals from the oxidizer.
- 10 2. The method of claim 1, further comprising maintaining a pH of the wastewater at a level at which the copper catalyzes the production of the hydroxyl radicals from the oxidizer.
3. The method of claim 1, further comprising obtaining the wastewater from a copper chemical mechanical polishing (CMP) operation of the semiconductor manufacturing facility.
- 15 4. The method of claim 1, wherein removing the one or more azoles from the wastewater includes removing one or more of 1,2,4-triazole, pyrazole, Benzotriazole, 5-methyl 1H-benzotriazole (Tolutriazole), or 3-amino 1,2,4-triazole from the wastewater.
- 20 5. The method of claim 1, wherein introducing the oxidizer into the wastewater includes introducing hydrogen peroxide into the wastewater.
6. The method of claim 5, further comprising obtaining the hydrogen peroxide from a waste stream from the semiconductor manufacturing facility.
- 25 7. The method of claim 1, wherein the copper is present in the wastewater in the form of copper sulfate.
8. A system for removing one or more azoles from copper-containing wastewater from a semiconductor manufacturing facility, the system comprising:
 - 30 a vessel fluidly connectable to a source of the wastewater;
 - a source of oxidizer configured to introduce the oxidizer into the wastewater in the vessel, the copper catalyzing production of hydroxyl radicals from the oxidizer to react with the one or more azoles; and

a source of pH adjustment chemical configured to introduce the pH adjustment chemical into the wastewater in the vessel.

9. The system of claim 8, further comprising:
5 a pH monitor disposed within the vessel; and
a controller configured to control the source of pH adjustment chemical to introduce the pH adjustment chemical into the wastewater in the vessel at a quantity and rate sufficient to maintain the pH of the wastewater at a level at which the copper catalyzes production of hydroxyl radicals from the oxidizer.
- 10
10. The system of claim 8, wherein the wastewater includes one or more of 1,2,4-triazole, pyrazole, Benzotriazole, 5-methyl 1H-benzotriazole (Tolutriazole), or 3-amino 1,2,4-triazole and the system is configured to decompose the one or more of 1,2,4-triazole, pyrazole, Benzotriazole, Tolutriazole, or 3-amino 1,2,4-triazole with the hydroxyl radicals.
- 15
11. The system of claim 8, wherein the wastewater is a copper chemical mechanical polishing (CMP) wastewater at the semiconductor manufacturing facility.
12. The system of claim 8, wherein the copper is in the form of copper sulfate.
- 20
13. The system of claim 8, wherein the source of oxidizer is a source of hydrogen peroxide.
14. The system of claim 13, wherein the source of hydrogen peroxide includes a waste
25 stream of the semiconductor manufacturing facility.