

SILICON CARBIDE (SiC) WAFER POLISHING WITH SLURRY FORMULATION AND PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to and is a non-provisional of U.S. Patent Application
5 63/188,305 (filed May 13, 2021), the entirety of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

Manufacturing hard wide band-gap materials is limited by the rate of silicon carbide (SiC) removal. To increase removal rates, one must enable the formation of a soft, yet dense, oxide layer at the surface of the silicon carbide material. This layer is removed by
10 mechanical abrasion (through hard abrasives and asperities on the surface of a polishing pad). Such mechanically abrasive processes tend to use very high working pressures and sliding velocities. The formation of this oxide layer is typically accomplished by the addition of the strong oxidizing agent potassium permanganate (KMnO_4) which weakens the surface forces on the silicon carbide substrate.

15 Due to the strong and corrosive nature of the permanganate, and also due to the fact that polishing equipment tends to get grossly discolored (*e.g.*, turn purple) after extended exposure to permanganate, there is a strong desire on the part of industry to activate the silicon carbide surface with less aggressive conditions that will also enhance removal rates, cause no discoloration, while decreasing the final number of substrate-level defects. To date,
20 no solution has been found to be entirely satisfactory.

The discussion above is merely provided for general background information and is not intended to be used as an aid in determining the scope of the claimed subject matter.

SUMMARY

A method for polishing a silicon carbide surface is provided. The silicon carbide
25 surface is polished with a particulate abrasive while exposed to a composition of water, an oxidizing agent and an electrophile. The method provides material removal rates (MRR) that are competitive with, or superior to, conventional methods without utilizing harsh chemicals. An advantage that may be realized in the practice of some disclosed embodiments of the method is providing a material removal rate that is competitive with, or superior to,
30 conventional KMnO_4 methods but which does not utilize such a strong, discoloring and corrosive reagent. The residual materials are also more environmentally friendly.

In a first embodiment, a method for polishing a silicon carbide surface is provided. The method comprising: exposing a silicon carbide surface to a composition comprising (1) water (2) an oxidizing agent (3) an electrophile and (4) a particulate abrasive; and polishing the silicon carbide surface while the silicon carbide surface is exposed to the composition.

5 In a second embodiment, a method for polishing a silicon carbide surface is provided. The method comprising: exposing a silicon carbide surface to a composition comprising (1) water (2) an oxidizing agent (3) a metal ion electrophile with a ligand and (4) a particulate abrasive; and polishing the silicon carbide surface while the silicon carbide surface is exposed to the composition.

10 This brief description of the invention is intended only to provide a brief overview of subject matter disclosed herein according to one or more illustrative embodiments, and does not serve as a guide to interpreting the claims or to define or limit the scope of the invention, which is defined only by the appended claims. This brief description is provided to introduce an illustrative selection of concepts in a simplified form that are further described below in
15 the detailed description. This brief description is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used as an aid in determining the scope of the claimed subject matter. The claimed subject matter is not limited to implementations that solve any or all disadvantages noted in the background.

BRIEF DESCRIPTION OF THE DRAWINGS

20 So that the manner in which the features of the invention can be understood, a detailed description of the invention may be had by reference to certain embodiments, some of which are illustrated in the accompanying drawings. It is to be noted, however, that the drawings illustrate only certain embodiments of this invention and are therefore not to be considered limiting of its scope, for the scope of the invention encompasses other equally effective
25 embodiments. The drawings are not necessarily to scale, emphasis generally being placed upon illustrating the features of certain embodiments of the invention. In the drawings, like numerals are used to indicate like parts throughout the various views. Thus, for further understanding of the invention, reference can be made to the following detailed description, read in connection with the drawings in which:

30 FIG. 1 is an illustration of activation of a silicon carbide surface using the disclosed method;

FIG. 2 depicts examples of non-metal electrophiles for use with the disclosed method;

FIG. 3 depicts examples of various ligands for use with metal ion electrophiles;

FIG. 4 is a graph depicting the material removal rate (MRR) of two non-metal electrophiles used with the disclosed method. Conventional ferro KMnO_4 MRR is shown in gray;

FIG. 5 is a graph depicting the material removal rate (MRR) of copper metal electrophiles used with four different ligands. Conventional ferro KMnO_4 MRR is shown in gray; and

FIG. 6 is a graph depicting the material removal rate (MRR) of vanadium metal electrophiles used with two different ligands. Conventional ferro KMnO_4 MRR is shown in gray.

10 DETAILED DESCRIPTION OF THE INVENTION

This disclosure provides slurry formulations for silicon carbide polishing with tunable performance upon the addition of certain additives that enhance removal rates under a less aggressive physicochemical environment. More specifically this disclosure provides formulations, as well as systems, that enhance the development of silicon carbide polishing processes and chemical-mechanical polishing (CMP) processes, including planarization, in particular.

Generally, the formulation comprises (1) water (2) a water-soluble electrophile (E^+) such as a metal ion chelated with a ligand via an Organometallic Complex Ligand Exchange (OMC-LE) or a non-metallic electrophile (3) an oxidizing agent (Ox) and (4) a particulate abrasive. The particulate abrasive, such as alumina is used at a pH above the isoelectric point (*e.g.* >2 , such as a pH 4-5 or a pH of 8-9) while a mechanical polishing force is applied (*e.g.* between 3 psi and 7psi (0.21 bar to 0.48 bar) applied by a rotating pad or brush). The abrasive is generally present in a concentration of about 2% to about 5% (wt/wt) and is water-insoluble. In one embodiment, the abrasive is alumina nanoparticles with an average

25 diameter of less than 100 nm. In one embodiment, the formulation consists of the water-soluble electrophile, the oxidizing agent and water. In another embodiment, the abrasives are nanoparticles of silica, zirconia, titania, diamond or a metal oxide. The polishing method is generally performed at room temperature (*e.g.* between 20°C and 25°C).

Without wishing to be bound by any particular theory, FIG. 1 depicts one possible mechanism to aid in understanding the disclosed method. Panel A of FIG. 1, shows an oxide surface of a silicon carbide substrate complexing with an water-soluble electrophile (E^+). The surface hydroxyl groups are deprotonated and highly anionic (*i.e.*, they serve as a nucleophile) within a complexation layer between the additive-surface interface resulting in

the weakening of the Si-C bonds. Panel B shows the activated surface being oxidizing by an oxidizing agent (Ox). In panel C, an abrasive (*e.g.* alumina) liberates the topmost silicon layer to produce the polished surface shown in panel D.

Examples of suitable oxidizing agents include hydrogen peroxide (H_2O_2), permanganate (*e.g.* KMnO_4 (KPS)) and persulfates such as ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$). Without wishing to be bound to any particular theory, these oxidizing agents are believed to generate hydroxyl radicals *in situ*. The oxidizing agent is generally present in a concentration between 1% and 10% by weight. In one embodiment, the oxidizing agent is present in a concentration between 1% and 5% by weight. In yet another embodiment, the oxidizing agent is present in a concentration between 2% and 4% by weight.

Referring to FIG. 2, in one embodiment, the water-soluble electrophile is a non-metallic electrophile such as an aldehyde, an acyl halide (or carboxylic acid therefrom) or a boron-based compound. Examples of boron-based compounds include boronic acids such as ethylboronic acid, cyclopentylboronic acid, isopropylboronic acid, cyclohexylboronic acid, cyclopentylboronic acid, p-tolylboronic acid, phenylboronic acid, borax, or boric acid. Other suitable boron-based compounds include boroglycine or borates such as trimethyl borate or triethylborate. Due to the electron deficient nature of these supramolecular molecules, an enhanced nucleophilic attack from the silicon carbide substrate can occur.

In the case of OMC-LE, the M^+ center of the organometallic complex acts as the electrophile which undergoes the nucleophilic attack from the silicon carbide substrate. Furthermore, the organometallic complex facilitates the *in situ* formation of hydroxyl radicals from the oxidizing agent.

Examples of suitable metal ions include group II metals such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and divalent transition metals such as Cu^{2+} , Zn^{2+} . Further examples of suitable metal ions include Fe^{3+} , Co^{3+} , Ti^{4+} , V^{4+} , V^{5+} , Cr^{6+} , Mo^{6+} and Mn^{7+} . Generally, the metal is water-soluble or is rendered water-soluble by complexation with the ligand or with a micelle. The metal is generally present in a concentration between 0.005% and 0.05% by weight. In another embodiment, the metal is present in a concentration between 0.005 and 0.015% by weight.

Referring to FIG. 3, examples of suitable ligands include amino acids (*e.g.* glycine, serine, arginine, cystine, phenylalanine, etc.), monoprotic carboxylic acids (*e.g.* formic acid, acetic acid, glycolic acid, propionic acid, butanoic acid, hexanoic acid, heptanoic acid, octanoic acid, decanoic acid, pyruvic acid, t-cinnamic acid, etc.) diprotic carboxylic acids (*e.g.* carbonic acid, itaconic acid, malonic acid, tartaric acid, etc.), carbamates (*e.g.* tert-butyl

N-(benzyloxy)carbamate), hydroxamic acids and hydroxamic esters (*e.g.* suberohydroxamic acid, salicylhydroxamic acid, ethyl acetohydroxamate), hydroxyurea and aliphatic amides (*e.g.* butyramide). Generally, the ligand is water-soluble. The ligand is present in a weight ratio of from about 1:5 to about 1:20 (metal:ligand). In another embodiment, the ligand is present in a weight ratio from about 1:8 to about 1:12 (metal:ligand). In yet another embodiment, the ligand is present in a weight ratio of 1:10 (metal:ligand).

The disclosed compositions are competitive with conventional ferro KMnO_4 polishing techniques and, in some cases, have a superior material removal rate (MRR). FIGS. 4-6 depict typical MRR for conventional KMnO_4 shown in gray.

FIG. 4 depicts a control (see Example 1), a boric acid example (see Example 11) and a borax example (see Example 12). Both the Cu-boric acid and Cu-borax examples outperformed conventional KMnO_4 MRR (shown in gray) under identical conditions.

FIG. 5 depicts a control (see Example 1), and three copper-ligand examples including a glycine ligand (Example 2), a serine ligand (example 3), a cystine example (Example 5) and a salicylhydroxamic acid example (example 6). The Cu-serine outperforms conventional KMnO_4 MRR (shown in gray) under identical conditions. The Cu-glycine, Cu-cystine and Cu-salicylhydroxamic acid is competitive with conventional KMnO_4 techniques but avoids the drawbacks associated with these conventional reagents.

FIG. 6 depicts a control (see Example 1) and two vanadium-ligand examples including a serine ligand (Example 7) and a tartaric acid ligand (Example 8). The V-serine example is competitive with conventional ferro KMnO_4 techniques but avoids the drawbacks associated with these conventional reagents. The V-tartaric acid example outperforms conventional KMnO_4 MRR (shown in gray) under identical conditions with nearly double the material removal rate (MRR).

Detailed Examples

All polishing trials were run on an Allied METPREP(TM) polisher, using a 100 mm diameter and a 350 mm thick 4H-SiC N-type wafer that was repeatedly re-polished. A Dupont SUBA(R) 800-II-12 X-Y grooved pad on a 200-mm rotating platen was used. The 3M (PB33A-1) bristle brush conditioning disc was used in an *in-situ* conditioning mode for the duration of the polish and for 1 minute during an *ex-situ* disc conditioning after the polish. The Si face of the wafer was polished for 10 minutes using a slurry that consisted of $\alpha\text{-Al}_2\text{O}_3$ nanoparticles (NPs), water, hydrogen peroxide, and the respective additives (organometallic complexes or electrophilic additives) as described in each example. The process pressure

ranged between 3 and 7 PSI. The relative sliding velocity ranged between 0.25 to 1.05 m/s. Slurry flow rate was kept constant at 25 cc per minute. Examples are summarized in Table 1.

Table 1						
Example	H ₂ O ₂ (wt %)	Al ₂ O ₃ (wt %)	E ⁺ (wt %)	E ⁺	Ligand (wt %)	Ligand
1	3	3	0	---	0	---
2	3	3	0.01	Cu ²⁺	0.1	glycine
3	3	5	0.01	Cu ²⁺	0.1	serine
4	3	3	0.01	Cu ²⁺	0.1	serine
5	3	3	0.01	Cu ²⁺	0.1	cystine
6	3	3	0.01	Cu ²⁺	0.1	salicylhydroxamic acid
7	3	3	0.01	V ⁴⁺	0.1	serine
8	3	3	0.01	V ⁴⁺	0.1	tartaric acid
9	3	3	0.02	V ⁴⁺	0.1	tartaric acid
10	3	3	0.005	V ⁴⁺	0.1	tartaric acid
11	3	3	1.0	boric acid	---	---
12	3	3	1.0	borax	---	---
13	5% ammonium persulfate	3	0.01	Cu ²⁺	0.1	Serine

Example 1 - Control (electrophile-free)

A silicon carbide (SiC) slurry comprised of 3% α -Al₂O₃ nanoparticles (NPs), water, and 3% hydrogen peroxide was used for the experiment. A Dupont SUBA(R) 800-II-12 X-Y grooved pad on a 200-mm rotating platen was used. The 3M (PB33A-1) bristle brush conditioning disc was used in an *in-situ* conditioning mode for the duration of the polish and for 1 minute during *ex-situ* conditioning after the polish. The silicon face of 4H-SiC N-Type wafers having a 100mm diameter and a thickness of 350 μ m were polished. Process pressure ranged between 3 and 7 PSI. Sliding velocity was kept constant at 1.05 m/s. Slurry flow rate was kept constant at 25 cc per minute.

The observed SiC removal rates ranged from 348 to 532 nanometers per hour. At 3 PSI, SiC removal rates averaged at 348 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 532 nanometers per hour, corresponding to an increase of 35% from the lower downforce.

Example 2 - Cu²⁺-glycine

Example 2 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% α -Al₂O₃ nanoparticles (NPs), water, 3% hydrogen peroxide, and Cu²⁺-glycine (0.01% metal, 0.1% ligand).

After polishing, and depending on the process conditions, the observed SiC removal rates ranged from 936 to 1,198 nanometers per hour. At 3 PSI, SiC removal rates averaged at 936 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 1,198 nanometers per hour, corresponding to an increase of 22% from the lower downforce. See FIG. 5.

Example 3 - Cu²⁺-serine with 5% alumina

Example 3 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 5% α -Al₂O₃ nanoparticles (NPs), water, 3% hydrogen peroxide, and Cu²⁺-serine (0.01% metal, 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rate of 1563 nanometers per hour at 7 PSI.

Example 4 - Cu²⁺-serine with 3% alumina

Example 4 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% α -Al₂O₃ nanoparticles (NPs), water, 3% hydrogen peroxide, and Cu²⁺-serine (0.01% metal 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates ranged from 1,371 to 1,709 nanometers per hour. At 3 PSI, SiC removal rates averaged

at 1,371 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 1,709 nanometers per hour, corresponding to an increase of 20% from the lower downforce. See FIG. 5.

Example 5 - Cu^{2+} -cystine

5 Example 5 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% $\alpha\text{-Al}_2\text{O}_3$ nanoparticles (NPs), water, 3% hydrogen peroxide, and Cu^{2+} -cystine (0.01% metal, 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates at 7 PSI, 1.05 sliding velocity and 25 cc/min flow rate was 883 nm/hr. See FIG. 5.

10 Example 6 - Cu^{2+} - salicylhydroxamic acid

Example 6 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% $\alpha\text{-Al}_2\text{O}_3$ nanoparticles (NPs), water, 3% hydrogen peroxide, and Cu^{2+} -salicylhydroxamic acid (0.01% metal, 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates at 7 PSI, 1.05 sliding velocity and 25 cc/min flow rate was 753 nm/hr. See FIG. 5.

Example 7 - V^{4+} -serine

Example 7 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% $\alpha\text{-Al}_2\text{O}_3$ nanoparticles (NPs), water, 3% hydrogen peroxide, and V^{4+} -serine (0.01% metal, 0.1% ligand).

20 After polishing and depending on the process conditions, the observed SiC removal rates ranged from 926 to 1,132 nanometers per hour. At 3 PSI, SiC removal rates averaged at 926 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 1,132 nanometers per hour, corresponding to an increase of 18% from the lower downforce. See FIG. 6.

25 Example 8 - V^{4+} -tartaric acid

Example 8 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% $\alpha\text{-Al}_2\text{O}_3$ nanoparticles (NPs), water, 3% hydrogen peroxide, and V^{4+} -tartaric acid (0.01% metal, 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates ranged from 1,837 to 2,152 nanometers per hour. At 3 PSI, SiC removal rates averaged at 1,837 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 2,152 nanometers per hour, corresponding to an increase of 15% from the lower downforce. See FIG. 6.

Example 9 - V^{4+} -tartaric acid

Example 9 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% α -Al₂O₃ nanoparticles (NPs), water, 3% hydrogen peroxide, and V⁴⁺-tartaric acid (0.02% metal, 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates at 7 PSI, 1.05 sliding velocity and 25 cc/min flow rate was 999 nm/hr.

Example 10 - V⁴⁺-tartaric acid

Example 10 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3% α -Al₂O₃ nanoparticles (NPs), water, 3% hydrogen peroxide, and V⁴⁺-tartaric acid (0.05% metal, 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates at 7 PSI, 1.05 sliding velocity and 25 cc/min flow rate was 1442 nm/hr.

Example 11 - boric acid

Example 11 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3.0% α -Al₂O₃ nanoparticles (NPs), water, 3.0% hydrogen peroxide, and 1.0% boric acid. See FIG. 4.

After polishing and depending on the process conditions, the observed SiC removal rates ranged from 1,427 to 1,904 nanometers per hour. At 3 PSI, SiC removal rates averaged at 1,427 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 1,904 nanometers per hour, corresponding to an increase of 25% from the lower downforce.

Example 12 - borax

Example 12 was substantially identical to Example 1 except in that the silicon carbide (SiC) slurry was comprised of 3.0% α -Al₂O₃ nanoparticles (NPs), water, 3.0% hydrogen peroxide, and 1.0% borax.

After polishing and depending on the process conditions, the observed SiC removal rates at 7 PSI, 1.05 sliding velocity and 25 cc/min flow rate was 2446 nm/hr. See FIG. 4.

Example 13 – ammonium persulfate

Example 13 was substantially identical to Example 1 except in that 5% ammonium persulfate was used instead of H₂O₂ and the pH was 4.0. The slurry comprised 3.0% α -Al₂O₃ nanoparticles (NPs), water, the aforementioned 5% (m/m) ammonium persulfate and Cu²⁺-serine (0.01% metal 0.1% ligand).

After polishing and depending on the process conditions, the observed SiC removal rates ranged from 1,162 to 1,408 nanometers per hour. At 3 PSI, SiC removal rates averaged at 1,162 nanometers per hour. A comparison at 7 PSI gave an average removal rate of 1,408 nanometers per hour.

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples
5 that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal language of the claims.

What is claimed is:

1. A method for polishing a silicon carbide surface, the method comprising:
exposing a silicon carbide surface to a composition comprising (1) water (2) an
oxidizing agent (3) an electrophile and (4) a particulate abrasive; and
5 polishing the silicon carbide surface while the silicon carbide surface is exposed to the
composition.
2. The method as recited in claim 1, wherein the electrophile is a boron-based
compound.
3. The method as recited in claim 1, wherein the electrophile is a boronic acid.
- 10 4. The method as recited in claim 1, wherein the electrophile is a boronic acid selected
from a group consisting of ethylboronic acid, cyclopentylboronic acid,
isopropylboronic acid, cyclohexylboronic acid, cyclopentylboronic acid, p-
tolylboronic acid, phenylboronic acid, borax, and boric acid.
5. The method as recited in claim 1, wherein the electrophile is boric acid or borate and
15 the oxidizing agent is hydrogen peroxide.
6. The method as recited in claim 1, wherein the electrophile is a borate.
7. The method as recited in claim 1, wherein the electrophile is a borate selected from a
group consisting of trimethyl borate and triethylborate.
8. The method as recited in claim 1, wherein the oxidizing agent is hydrogen peroxide.
- 20 9. The method as recited in claim 1, wherein the oxidizing agent is a persulfate.
10. The method as recited in claim 1, wherein the oxidizing agent is ammonium
persulfate.
11. The method as recited in claim 1, wherein the oxidizing agent is present in the
composition at a concentration between 1% and 10% by weight.
- 25 12. The method as recited in claim 1, wherein the oxidizing agent is present in the
composition at a concentration between 1% and 5% by weight.
13. The method as recited in claim 1, wherein the oxidizing agent is present in the
composition at a concentration between 2% and 4% by weight.
14. The method as recited in claim 1, wherein the composition consists of the water, the
30 oxidizing agent, the electrophile and the particulate abrasive.
15. The method as recited in claim 1, wherein the electrophile is an aldehyde, an acyl
halide or a carboxylic acid.
16. A method for polishing a silicon carbide surface, the method comprising:

exposing a silicon carbide surface to a composition comprising (1) water (2) an oxidizing agent (3) a metal ion electrophile with a ligand and (4) a particulate abrasive; and
 polishing the silicon carbide surface while the silicon carbide surface is exposed to the composition.

17. The method as recited in claim 16, wherein the oxidizing agent is hydrogen peroxide.
18. The method as recited in claim 16, wherein the metal ion electrophile is a divalent metal ion selected from a group consisting of Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , Zn^{2+} .
19. The method as recited in claim 16, wherein the metal ion electrophile is Cu^{2+} .
20. The method as recited in claim 16, wherein the metal ion electrophile is selected from a group consisting of Fe^{3+} , Co^{3+} , Ti^{4+} , V^{4+} , V^{5+} , Cr^{6+} , Mo^{6+} and Mn^{7+} .
21. The method as recited in claim 16, wherein the metal ion electrophile is selected from a group consisting of Co^{3+} , Ti^{4+} , V^{4+} , V^{5+} , Cr^{6+} , Mo^{6+} and Mn^{7+} .
22. The method as recited in claim 16, wherein the metal ion electrophile is V^{4+} or V^{5+} .
23. The method as recited in claim 16, wherein the ligand is an amino acid.
24. The method as recited in claim 16, wherein the ligand is an amino acid selected from a group consisting of glycine, serine, arginine, cystine and phenylalanine.
25. The method as recited in claim 16, wherein the ligand is a monoprotic carboxylic acid.
26. The method as recited in claim 16, wherein the ligand is a monoprotic carboxylic acid selected from a group consisting of formic acid, acetic acid, glycolic acid, propionic acid, butanoic acid, hexanoic acid, heptanoic acid, octanoic acid, decanoic acid, pyruvic acid and t-cinnamic acid.
27. The method as recited in claim 16, wherein the ligand is a diprotic carboxylic acid.
28. The method as recited in claim 16, wherein the ligand is a diprotic carboxylic acid selected from a group consisting of carbonic acid, itaconic acid, malonic acid and tartaric acid.
29. The method as recited in claim 16, wherein the ligand is tartaric acid.
30. The method as recited in claim 16, wherein the ligand is a carbamate.
31. The method as recited in claim 16, wherein the ligand is a hydroxamic acid or a hydroxamic ester.
32. The method as recited in claim 16, wherein the ligand is a hydroxamic acid or a hydroxamic ester selected from a group consisting of suberohydroxamic acid, salicylhydroxamic acid and ethyl acetohydroxamate.

33. The method as recited in claim 16, wherein the ligand is an aliphatic amide.
34. The method as recited in claim 16, wherein the ligand is hydroxyurea.
35. The method as recited in claim 16, wherein the composition consists of the water, the oxidizing agent, the metal ion electrophile and the particulate abrasive.
- 5 36. The method as recited in claim 16, wherein the oxidizing agent is hydrogen peroxide, the metal ion electrophile is V^{4+} , and the ligand is tartaric acid.