[0006] Looking first to FIG. 1A (prior art), an example embodiment 100 is provided for the traditional etch approach. A liquid etch solution 106 is applied to a material 104 on the surface of a substrate 108 for a microelectronic workpiece. For the example embodiment 100, the material 104 being etched is a cobalt (Co), and this material 104 has been previously formed on the surface of the substrate 108. For the example embodiment 100, the liquid etch solution 106 provides an oxidation-dissolution etch mechanism. For this oxidation-dissolution etch mechanism, the material 104 is oxidized by the liquid etch solution 106 and then dissolved by the liquid etch solution 106.

[0007] The traditional oxidation-dissolution etch mechanism for cobalt leads to significant roughening and pitting. For this traditional approach, cobalt etch is driven by an oxidation/dissolution mechanism where the oxidant (*e.g.*, hydrogen peroxide) oxidizes cobalt (Co) to form CoO_x with an oxidation rate constant of k_{ox} as represented by arrow 110. CoO_x is then dissolved into the solution through complexation with etchant molecules (*e.g.*, citrate anions) with a dissolution rate constant of k_d as represented by arrow 112. For this traditional approach, k_{ox} is less than k_d ($k_{ox} < k_d$), and this condition results in non-uniform etch at grain boundaries for the polycrystalline cobalt leading to pitting and roughening of the surface.

[0008] FIG. 1B (prior art) provides a representative surface image 150 for this pitting and roughening of a surface due to the undesired etch variability associated with the traditional oxidation-dissolution approach. In contrast, an ideal wet etch process would provide a constant etch rate independent of the surface chemistry (*e.g.*, grain boundaries) of the material being etched.

SUMMARY

[0008a] According to a first aspect of the present invention, there is provided a method of processing a substrate for a microelectronic workpiece, comprising:

receiving a substrate for a microelectronic workpiece having a polycrystalline material to be etched from a surface of the substrate;

applying an etch solution to the surface of the substrate, the etch solution having a first level of reactants with respect to the polycrystalline material;

exposing the etch solution and the surface of the material to illumination to form

an oxidized layer of material on the surface of the polycrystalline material, the exposing causing the etch solution to have a second level of reactants with respect to the polycrystalline material that is greater than the first level; and

removing the oxidized layer of material by dissolving, wherein the oxidizing having an oxidation rate constant greater than a dissolution rate constant for the dissolving.

[0008b] According to a second aspect of the present invention, there is provided a method of processing a substrate for a microelectronic workpiece, comprising:

receiving a substrate for a microelectronic workpiece having a polycrystalline elemental metal to be etched from a surface of the substrate;

applying a liquid etch solution comprising hydrogen peroxide to the surface of the substrate, the liquid etch solution having a first level of reactants with respect to the polycrystalline elemental metal;

illuminating the liquid etch solution to cause formation of hydroxyl radicals from the hydrogen peroxide, the formation of hydroxyl radicals at least in part causing the liquid etch solution to have a second level of reactants with respect to the polycrystalline elemental metal, the second level of reactants being greater than the first level of reactants;

oxidizing the polycrystalline elemental, metal with the liquid etch solution to form an oxidized metal; and

removing the oxidized metal by dissolving, wherein the oxidizing having an oxidation rate constant greater than a dissolution rate constant for the dissolving.

[0008c] According to a third aspect of the present invention, there is provided a method to polish a surface of a material, comprising:

receiving a polycrystalline elemental metal material to be polished;

applying an etch solution to a surface of the polycrystalline elemental metal material, the etch solution having a first level of reactants with respect to the polycrystalline elemental metal material;

exposing the etch solution and the surface of the polycrystalline elemental metal material to illumination to form an oxidized layer of material on the surface of the polycrystalline elemental metal material, the exposing causing the etch solution to have a second level of reactants with respect to the polycrystalline elemental metal material that is greater than the first level; and

removing the modified oxidized layer of material by dissolving to cause the polycrystalline elemental metal material to have a polished surface, the polished surface having less surface variation than the surface of the polycrystalline elemental metal material before the exposing and removing, wherein the oxidizing having an oxidation rate constant greater than a dissolution rate constant for the dissolving.

[0009] Embodiments are described herein that use illumination of etch solutions to provide controlled etching of materials. For one embodiment, disclosed methods include depositing etch solutions (*e.g.*, at least one of gaseous etch solution, a liquid etch solution, or a combination thereof) over a material where the etch solutions contain reactants to react with the material surface, ultimately leading to etching of the material. The material being etched can be, for example, a polycrystalline material, a polycrystalline metal, and/or other material to be etched or polished. The disclosed embodiments use illumination as an external tool to control etchant reactivity in the etch solution contacting the material, thereby allowing for modifications to the etch behavior. Chemical composition as well as other parameters can also

CLAIMS

1. A method of processing a substrate for a microelectronic workpiece, comprising:

receiving a substrate for a microelectronic workpiece having a polycrystalline material to be etched from a surface of the substrate;

applying an etch solution to the surface of the substrate, the etch solution having a first level of reactants with respect to the polycrystalline material;

exposing the etch solution and the surface of the material to illumination to form an oxidized layer of material on the surface of the polycrystalline material, the exposing causing the etch solution to have a second level of reactants with respect to the polycrystalline material that is greater than the first level; and

removing the oxidized layer of material by dissolving, wherein the oxidizing having an oxidation rate constant greater than a dissolution rate constant for the dissolving.

2. The method of claim 1, wherein the etch solution comprises at least one of gaseous etch solution, a liquid etch solution, or a combination thereof.

3. The method of claim 1, further comprising repeating the exposing and removing in a cyclic manner to etch the material.

4. The method of claim 1, wherein the exposing and removing are performed in at least one of a single process step or different process steps.

5. The method of claim 1, wherein the etch solution comprises a liquid etch solution.

6. The method of claim 5, wherein the removing comprises using the liquid etch solution in a separate process step to dissolve the oxidized material.

7. The method of claim 5, wherein the etch solution comprises an aqueous solution including hydrogen peroxide, and wherein the removing comprises using an aqueous solution including a complexing agent.

8. The method of claim 7, wherein the complexing agent comprises at least one of citrate, ethylene diamine, ethylendiamintetraacetate (EDTA), malic acid, oxalic acid, glycine, alanine, or iminodiacetic acid.

9. The method of claim 5, wherein the removing comprises dissolving the oxidized material using the liquid etch solution simultaneously with the oxidizing.

10. The method of claim 9, wherein the liquid etch solution comprises an aqueous solution including hydrogen peroxide and citrate.

11. The method of claim 5, wherein the polycrystalline material to be etched comprises a polycrystalline elemental metal, and wherein the polycrystalline elemental metal comprises cobalt.

12. The method of claim 5, wherein the liquid etch solution comprises hydrogen peroxide.

13. The method of claim 12, wherein the illuminating of the hydrogen peroxide causes formation of hydroxyl radicals within the liquid etch solution, wherein the second level of reactants are caused at least in part by the formation of the hydroxyl radicals, and wherein the hydroxyl radicals oxidize the material.

14. The method of claim 13, wherein the illuminating comprises illuminating the liquid etch solution with light having at least one of a wavelength of less than 560 nm or a wavelength from 10 nm to 400 nm.

15. The method of claim 1, wherein the exposing comprises selectively illuminating the etch solution.

16. The method of claim 15, wherein the selectively illumination comprises illuminating with ultraviolet WV) light in one or more on/off patterns.

17. The method of claim 15, wherein the selectively illuminating comprises illuminating with two or more different colors of light, and wherein the removing comprises using two or more different colors of light to illuminate the modified layer of material.

18. The method of claim 15, wherein the selectively illuminating comprises illuminating one or more regions of the etch solution where the oxidized layer is desired and not illuminating other regions of the etch solution.

19. The method of claim 1, wherein the etch solution comprises an aqueous solution including at least one of ozone or hypochlorous acid.

20. The method of claim 1, further comprising adjusting the exposing so that different regions of the etch solution are exposed differently to provide different amounts of etching within the different regions.

21. The method of claim 20, further comprising measuring the polycrystalline material and controlling the adjusting based upon the measuring to provide feed-forward control, and wherein the measuring comprises measuring at least one of a topology for a surface of the polycrystalline material or a thickness of the polycrystalline material.

22. A method of processing a substrate for a microelectronic workpiece, comprising:

receiving a substrate for a microelectronic workpiece having a polycrystalline elemental metal to be etched from a surface of the substrate;

applying a liquid etch solution comprising hydrogen peroxide to the surface of the substrate, the liquid etch solution having a first level of reactants with respect to the polycrystalline elemental metal;

illuminating the liquid etch solution to cause formation of hydroxyl radicals from the hydrogen peroxide, the formation of hydroxyl radicals at least in part causing the liquid etch solution to have a second level of reactants with respect to the polycrystalline elemental metal, the second level of reactants being greater than the first level of reactants;

oxidizing the polycrystalline elemental, metal with the liquid etch solution to form an oxidized metal; and

removing the oxidized metal by dissolving, wherein the oxidizing having an oxidation rate constant greater than a dissolution rate constant for the dissolving.

23. The method of claim 22, further comprising repeating the illuminating, oxidizing, and removing to etch the polycrystalline elemental metal.

24. The method of claim 22, wherein the removing comprises dissolving the oxidized metal using the liquid etch solution simultaneously with the oxidizing.

25. A method to polish a surface of a material, comprising:

receiving a polycrystalline elemental metal material to be polished;

applying an etch solution to a surface of the polycrystalline elemental metal material, the etch solution having a first level of reactants with respect to the polycrystalline elemental metal material;

exposing the etch solution and the surface of the polycrystalline elemental metal material to illumination to form an oxidized layer of material on the surface of the polycrystalline elemental metal material, the exposing causing the etch solution to have a second level of reactants with respect to the polycrystalline elemental metal material that is greater than the first level; and

removing the modified oxidized layer of material by dissolving to cause the polycrystalline elemental metal material to have a polished surface, the polished surface having less surface variation than the surface of the polycrystalline elemental metal material before the exposing and removing, wherein the oxidizing having an oxidation rate constant greater than a dissolution rate constant for the dissolving.

26. The method of claim 25, wherein the etch solution comprises at least one of gaseous etch solution, a liquid etch solution; or a combination thereof.

27. The method of claim 25, further comprising repeating the exposing and removing in a cyclic manner to polish the material.