

[SPECIFICATION]

[Name of Invention]

Preparation method of Ruthenium(Ru) powder for preparation of Ruthenium target

[Technological Field]

The present invention is related to a producing method of Ruthenium(Ru) raw material powder used in manufacturing a target or other Ru compound. In particular, the present invention is related to a producing method of Ru powder material, wherein Ruthenium(Ru) oxide is produced by applying a heat process to high purity powder produced by plasma, Ru oxide is changed into a refined shape through pulverization, high purity Ru powder is produced through an atmospheric heat process and thereby, a production yield and purity of powder can be improved. Finally, recently, a large capacity and a high integrity related to a magnetic recording medium or next-generation memory are required very eagerly. In order to meet this requirement, the present invention provides a producing method of Ru powder material which is widely used in a seed layer for forming a magnetic layer.

[Background of Invention]

The present invention is related to a producing method of high purity Ru powder, wherein coarse powder is produced by applying plasma to a waste Ru target, Ru oxide is generated through a heat process, refined powder is finally acquired through a pulverization process, and high purity powder is produced through an atmospheric heat process. In particular, the present invention is related to a producing method of refined powder, wherein a production time is reduced, content of impure substances in powder can be controlled, Ru powder is produced by using plasma, and refined powder having a particle size of below 5 μ m through a pulverization process is produced.

Generally, in order to form an electrode layer of the next-generation semiconductor memory(RAM, MRAM, FeRAM) or a seed layer, a Ru thin film is frequently used. Further, since Ru powder for manufacturing a Ru sputtering target for a thin film molding is very expensive, Ru powder is produced by recycling a waste Ru target. A degree of purity is deteriorated due to continuous recycling of Ru. In order to prevent deterioration of purity and to easily control a thickness of a thin film, a technology for refining a crystal particle of a target and for producing high purity powder is required eagerly. A Ru target having refined crystal particles and high functionality is produced through a sintering process, and

refined and high purity Ru powder is demanded in order to control crystal particles.

Generally, a Ru target requires high purity and this requirement is to be satisfied to improve a degree of uniformity of a thin film. For this purpose, simplification of processes are required and gas content is also controlled so as to prevent impure substances not to be introduced during the whole processes. But, in connection with most methods such as a wet method or a dry method and so on, in particular, production of powder using an electrical explosion method, a plasma method and the like, in stead of the wet method using acids employs a post heat process for selectively removing carbon which is mixed with Ru by using mainly a carbon mold. The oxygen content is increased through this heat process. Particling is formed on the properties of a thin film because of increase of oxygen and thus, fatal defects are generated.

Recently, in order to compensate the shortcoming that oxygen content increases, a manufacturing method of Ru powder using pulverization has been attempted. For example, Japanese Patent Laid-Open Publication No. 2009-108400 discloses a manufacturing method using a waste Ru target, wherein powder is produced through a rough pulverization, a hammer milling, deposition and extraction, a magnetic selection, a dry process, deoxidizing and a heat process. However, if the method of the above-mentioned patent is used, it can solve the problems that much quantity of acid solution is used in a conventional wet method and oxygen content increases in the dry method. Further, the production time of powder can be shortened. But, in a case that a pulverization process is performed by a pulverization tool when pulverization(a rough pulverization and refined pulverization) applied for pulverizing a target of enormous size and processing it into refined shape is executed from the initial stage of a production process, pollution of tool component is generated in powder and a refining process of a metal, Ru is not executed smoothly and easily because of properties of the metal. Thus, there is a demerit that the production yield becomes low.

Further, even when evaporation/condensation is executed by using a plasma method, it is possible to produce high purity and refined powder of Nanometer Scale. But, there are problems that an yield rate is low when mass production is required and a process cost becomes terribly expensive because Ru has a very high evaporation point. Further, in case of powder of Nanometer Scale, it can be easily condensed in a post heat process. Therefore, handling is much difficult in a sintering process. Rather, powder of Micrometer Scale can be more easily handled in a sintering process as compared with powder of the Nanometer Scale.

[Contents of Invention]

[Technological Objects]

The present invention is related to a manufacturing method of high purity and refined Ru powder by using waste Ru target. The present invention employs an eco-friendly dry method instead of a conventional wet method. That is, the object of the present invention is to produce high purity powder by using plasma, and to finally produce high purity and refined Ru powder by increasing a production yield of powder when a refined pulverization process is executed, and preventing a degree of purity of powder from being deteriorated. When powder is produced in this way, it is possible to produce high purity and refined Ru powder on a large scale.

To be more specific, the object of the present invention is to produce coarse powder through a forced dispersing process, instead of evaporated/condensed powder of Nano Scale when producing high purity of powder by using a plasma device, and to finally produce ultra high purity and refined Ru powder by applying a refined pulverization process and a heat process to the produced powder.

[Technological Solution]

The present invention is characterized in that it produces coarse powder by forcibly dispersing a waste Ru target by using a plasma device, Ru oxide is acquired through an oxidation process at the same time carbon is removed for easily performing a refined pulverization process, and ultra high purity powder can be produced by applying an atmospheric heat process to the finally oxidized powder.

[Advantageous Effects]

As mentioned above, in case of a conventional wet method, complicated processes(wet dissolution, condensing, a dry process and a heat process) are performed and thus it takes several days to complete the processes. Further, there are many drawbacks that handling the processes are restricted due to the strong acid solution and the cost is generated because of treatment of waste solution.

Further, there are demerits that pollution is generated due to rough pulverization even in case of the dry method which is recently published, or terribly refined powder can be easily condensed by a post heat process when a plasma method is employed.

But, the present invention has the merits as follows. When producing refined and high purity Ru powder, powder is produced by forcibly dispersing ingots by using plasma. Thus a wet process can be omitted and pulverization can be easily performed by oxidizing coarse powder into a metal oxide. Through these processes, a production time of the final powder can be reduced and refined and high purity Ru powder can also be produced. Thus, functional improvement of a Ru sputtering target material produced by a sintering method is expected.

[Brief Description of Drawings]

FIG. 1 is a diagram illustrating a working procedure for producing Ru powder by using a waste Ru target of the present invention.

FIG. 2 is a diagram illustrating FESEM image of final Ru powder produced according to the present invention.

[Best Mode for realizing Invention]

The present invention provides a manufacturing method of Ru powder comprising a step for removing pollutants remaining on a surface of a waste Ru target and washing the surface; a step for forming a plasma atmosphere by decompressing an inside of a plasma device, injecting a reaction gas, and applying electricity after introducing the washed waste Ru target into the plasma device; a step for producing Ru powder by increasing a plasma electricity and then, forcibly dispersing ingots; a step for selectively removing carbon by applying an atmospheric heat process to the produced Ru powder in order to produce Ru oxide(RuOx) powder; a step for pulverizing the produced Ru oxide(RuOx) powder into refined shape for producing refined Ru powder; and a step for producing high purity Ru powder by applying a hydrogen atmospheric heat process to the produced Ru oxide(RuOx) powder.

[Embodiments of Invention]

When producing Ru powder by using a waste Ru target, the present invention is characterized in that when producing Ru powder, powder is produced by forcibly dispersing ingots by using plasma and thereby, coarse high purity powder is produced, a metal oxide is produced through a heat process, carbon which is mixed with Ru is selectively removed and simultaneously, pulverization can be easily executed, powder is pulverized into refined powder having an average particle size of 5 μ m through a refined pulverization process, and a

final refined and high purity Ru powder is produced through an atmospheric heat process. Through these processes, the processing time is reduced remarkably and condensation generated due to a heat process is suppressed as compared with a conventional plasma method. Therefore, it is possible to produce Ru powder which is suitable for refined and high purity sinter. Further, it is also possible to realize a production yield more than 95% and to produce powder having an average particle size of 5 μ m.

Below, a production method of the final powder is illustrated in FIG. 1.

The present invention is characterized in that it includes a step(S10) for removing pollutants remaining on a surface of a waste Ru target by using a chemical method and washing the surface; a step(S20) for forming a plasma atmosphere by decompressing an inside of a plasma device, injecting a reaction gas, and applying electricity after introducing the washed waste Ru target into the plasma device; a step(S30) for producing Ru powder by increasing a plasma electricity and then, forcibly dispersing ingots; a step(S40) for selectively removing carbon by applying an atmospheric heat process to the produced Ru powder in order to produce Ru oxide(RuOx) powder; a step(S50) for pulverizing the produced Ru oxide(RuOx) powder into refined shape for producing refined Ru powder; and a step(S60) for producing high purity Ru powder by applying a hydrogen atmospheric heat process to the produced Ru oxide(RuOx) powder.

Below, the above-mentioned processes are explained in detail.

First of all, pollutants remaining on a surface of a waste Ru target are removed(S10).

Surface pollution remains on a surface of a used waste Ru target due to handling. Thus, when producing powder by using the waste Ru target immediately after removal, it is possible to remove some pollutants through a plasma process, but there is a high possibility that the pollutants may remain in Ru powder which is being produced. This demerit acts as one factor to reduce quality of a final target and it is possible that the remaining pollutants are removed prior to the powder production processes. In removing the pollutants, a chemical method wherein a waste Ru target is deposited in a solvent for a short time, and a surface side is cut by several tens of μ m is employed, or a physical method including the mechanical processing methods such as a lathe or a grinding machine or MCT and the like. Thereby, a constant thickness layer is removed. When pollutants are removed by the mechanical processing methods, it is possible to remove a thickness of approximately 10 μ m. The main reason of it is that an oxidation layer may not be removed completely if the thickness to be removed is too thin and yield of the final powder may be reduced if the

thickness to be removed is too thick.

A plasma atmosphere is formed by decompressing an inside of a plasma device, injecting a reaction gas, and applying electricity after introducing the waste Ru target in which pollutants are removed into the plasma device(S20).

It is possible to wash inside of a chamber before a plasma process, so that impurities or foreign material can not be mixed or introduced. A waste Ru target is mounted on the mold of the washed inside of the chamber and the distance between a plasma torch and a target is adjusted. The material of an electrode used for forming plasma is very important and it is also important to minimize contamination. Molybdenum (Mo), Tungsten(W), Copper(Cu), Graphite, and Ruthenium(Ru) can be used as an anode mold material. It is important to minimize contamination due to a mold in order to prevent a degree of purity of a final powder from being deteriorated. Even if contamination is generated due to a mold, it is very essential to select a mold in which pollution can be easily removed. For realizing this purpose, it is possible that a carbon for which pollution can be easily removed is very advantageous. More preferably, even if pollution is generated, it is possible to use a high purity Ru mold which does not affect a degree of purity at all.

Molybdenum(Mo), Tungsten(W) and Ruthenium(Ru) can be used as a cathode mold material used in a plasma process. It is possible to use Ru of the same material for producing high purity powder.

Plasma is formed by decompressing an inside of a plasma device, injecting a reaction gas, and applying electricity. A pressure is reduced to 10^{-1} torr by a vacuum pump in order to form plasma, a reaction gas is injected and a working vacuum degree is adjusted. Then, electricity is provided. Ar, H₂, N₂, CH₄, or the mixed gases such as Ar+H₂, and Ar+N₂ can be used as a reaction gas. There is a high possibility that H₂, N₂, and O₂ remain in a final Ru powder. Thus, when H₂, N₂, O₂ are manufactured as a target for use in a semiconductor line, they affect a process for forming particles during a film forming process. As a result, it is most beneficial to employ Ar of ultra high purity. Even if it is possible to use H₂ or N₂ or as a reaction gas in order to increase a powder manufacturing speed, or a gas component remains in the produced powder due to O₂ remaining in a chamber, since it is possible to remove the remaining gas completely through a degassing process after processing the powder into refined shape, it is also possible to select a gas according to a working environment.

It is possible that the working vacuum level is set at approximately 100-300 torr. If the level is below 100 torr, the amount of inert gas required for forming plasma is very small. Thus, a direct transfer of heat is difficult. If the level is above 300 torr, a forced dispersing due to plasma is not almost formed.

It is possible that a vacuum level is adjusted through other cooling gas element attached to a device or a vacuum level control valve.

After forming plasma, Ru is produced by increasing electricity and forcibly dispersing ingot. Then, Ru oxide(RuOx) powder is produced by selectively removing carbon through a heat process(S30, S40).

If electricity provided to plasma is increased, a molten metal is formed, and dissociated plasma is forcibly discharged while the temperature of the molten metal is being increased. Then, Ru powder is forcefully dispersed from the molten metal. Such dispersed powder forms a circular hollow inside and the particle size of powder having 10-300 μ m is produced. At this time, it is possible that power of powder is below 10-50kw. If it is below 10kw, the power is low and thus the molten metal is not formed. Considering security of equipments and control of evaporation reaction, the processes are performed at below 50kw.

If CH₄ is used as a reaction gas and a mold is graphite(C) in order to increase a production speed of powder, carbon is introduced into produced powder. At this time, it is possible that carbon is removed by an atmospheric heat process.

The object of the atmospheric heat process is to remove carbon and to easily pulverize powder into refined shape by forming a Ru oxide.

Regarding a heat process condition, in case of the atmospheric heat process, it is possible that a heat process is performed at a temperature of 800-1200 $^{\circ}$ C for 1-5 hours. There is a high possibility that the remaining carbon may not be removed sufficiently and sufficient oxidization may not be realized if a temperature is below 800 $^{\circ}$ C and the process time is below 1 hour. There is a high possibility that produced powder may be condensed if a temperature is above 1200 $^{\circ}$ C and the process time is above 5 hours.

Refined Ru powder is produced by pulverizing the produced Ru oxide(RuOx) powder(S50). Ru powder undergoing the atmospheric heat process are pulverized into refined shape. At this time, it is possible to employ Jet-Mill, Planetary Mill and Ball Mill as a pulverization method. It is to be understood that Jet-Mill can be used as a pulverization method. The

main reason of it is that Jet-Mill method has the most strong pulverization power and introduction of impure substances can be easily and most wonderfully controlled.

Pure Ru metal is not pulverized even by Jet-Mill, but pulverization is performed very smoothly and easily in case of Ru oxide(RuOx). It is possible that the rotation speed of an inside classifier of Jet-Mill ranges from 1500 RPM to 15,000 RPM. If the speed becomes below 1,500 RPM, the particle size of powder is becoming too coarse. If the speed becomes above 15,000 RPM, the production yield of powder is reduced tremendously and remarkably. In particular, if the particle size of powder is too refined during a subsequent atmospheric heat process, inert energy is reduced and thus, condensation of powder is generated. If the particle size of powder is too coarse, the crystal particle size of a final target increases. Therefore, it is most possible that a particle size of powder becomes approximately 5 μ m according to the experiment results.

High purity Ru powder is produced by applying a hydrogen atmosphere heat process to the refined Ru oxide powder(S60).

The minutely pulverized Ru oxide powder is deoxidized and becomes high purity Ru powder through a hydrogen atmosphere heat process. At this time, it is possible that a heat process is performed at the temperature of 800-1200 $^{\circ}$ C for 1-5 hours. The main reason of it is as follows. In a case that a heat process is performed at temperature below 800 $^{\circ}$ C and for less than 1 hour, deoxidization of Ru oxide is not realized sufficiently. In a case that a heat process is performed at temperature above 1,200 $^{\circ}$ C and for more than 5 hours, there is a high possibility that powders may be condensed. At this time, it is possible that oxygen content contained in the deoxidized Ru powder becomes below 600 ppm. It is more possible that target of high density can be produced when sintering is performed if the oxygen content is below 400ppm. A reaction surface space is increased by performing a hydrogen atmosphere heat process and thus, the oxygen content in Ru powder is controlled so that high purity Ru powder can be produced.

[Embodiment 1]

1kg of a Ru target having a degree of purity of 3N5 was prepared in order to produce Ru powder. A chemical process was applied to a waste Ru target from which foreign substances were removed by using a heat plasma device of 100kw class, and thereby, Ru powder of 800g was produced. The process procedures and the conditions are as follows.

First of all, a target is placed on a carbon mold and then, is mounted on an equipment. Subsequently, a pressured is reduced to 1×10^{-1} torr by using a rotary pump and then, an atmosphere is formed by N_2 gas. Plasma of 20kw is applied to the atmosphere by using plasma of a mixed gas including Ar+ N_2 . Ru powder produced in this way has a shape of a hollow center and has a particle size of 10-300 μ m. Carbon contained in powder is removed through an atmospheric heat process at 850 $^{\circ}$ C for producing a Ru oxide. The Ru oxide powder is produced by Jet-Mill under a condition such as 300g/hr and thereby, the average particle size of 5.2 μ m is acquired. The powder acquired in this way is processed through a hydrogen atmosphere heat process at 850 $^{\circ}$ C for 4 hours and thus, a pure Ru powder can be produced. As a result of analyzing the pure Ru powder acquired as above through ICP(Induction Coupled Plasma) method, it is confirmed that it is a high purity powder having above 3N8. Further, it is confirmed through a gas analyzer that an oxygen content is 380ppm. As a result, it is to be understood that purity of powder is improved as a whole. Theses results are indicated in table 1 and 2. FE-SEM photos of a finally produced powder are illustrated in FIG. 2.

[table 1]

Impurities	Embodiment 1
Na	2.6
K	28
Th	0.0005
U	0.0001
Fe	18
Cr	11
Ni	4.5
Co	1.2
Cu	0.22
Al	0.96
Cl	14
Total of impurities(O is excluded)	168,023

Final degree of purity	99.983
------------------------	--------

* Unit of Impurities : ppm

* Other Impurities : Li, Be, Sc, V, Mn, Co, Ga, Ge, As, Se, Br, Rb, Sr, Nb, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, Hf, Ta, Au, Hg, Pb, Bi, and R

[table 2]

Impurities	Embodiment 1
O	80
N	2
H	1
C	7
S	0

[Comparison Example 1]

Ru powder having a shape of a hollow center is produced by applying plasma to the target which is same as the specification described in the embodiment 1. An atmospheric heat process is applied to the powder acquired in this manner at 850℃ for 4 hours. Therefore, carbon is removed and Ru oxide is formed. Once again, a hydrogen atmosphere heat process is applied to the power at 850℃ for 4 hours, so that Ru deoxidization can be realized. It turned out that the final particle size of Ru powder acquired in this way is 10-300μm and the oxygen content is 2,000ppm. As is apparent from this fact, it is to be understood that deterioration of purity is generated.

[Comparison Example 2]

Ru powder having a shape of a hollow center is produced by applying plasma to the target which is same as the specification described in the embodiment 1. After pulverizing the Ru powder having a shape of a hollow center by using Jet-Mill under the condition same as that described in the embodiment 1, an atmospheric heat process is applied to the Ru powder at 850℃ for 4 hours. Then, a hydrogen atmosphere heat process is applied to the Ru power at 850℃ for 4 hours for acquiring final powder. It turned out that the particle size of Ru

powder acquired in this way is 9.4 μ m and the oxygen content is 1,500ppm.

[Industrial Applicability]

According to the present invention, when producing high purity and refined Ru powder, ingot is forcibly dispersed by using plasma for producing powder. It is possible to omit a wet process and it is also possible to easily perform pulverization by changing coarse powder into a metal oxide. Through these processes, the production time of a final powder can be shortened. Further, high purity and refined Ru powder can be produced. Therefore, it is expected that a function of a Ru sputtering target material produced according to a sintering method is improved.

[Claims]

1. A manufacturing method of Ru(Ruthenium) powder comprising,
 - (a) a step for removing pollutants remaining on a surface of a waste Ru target and washing the surface;
 - (b) a step for forming a plasma atmosphere by decompressing an inside of a plasma device, injecting a reaction gas, and applying electricity after introducing the washed waste Ru target into the plasma device;
 - (c) a step for producing Ru powder by increasing a plasma electricity and then, forcibly dispersing ingots;
 - (d) a step for selectively removing carbon by applying an atmospheric heat process to the produced Ru powder in order to produce Ru oxide(RuOx) powder;
 - (e) a step for pulverizing the produced Ru oxide(RuOx) powder into refined shape for producing refined Ru powder; and
 - (f) a step for producing high purity Ru powder by applying a hydrogen atmospheric heat process to the produced Ru oxide(RuOx) powder.
2. The manufacturing method of Ru powder according to the claim 1, wherein an inside pressure of the device is 100-300 torr in the step for forming plasma, and any one selected from Ar, H₂, N₂, or O₂ or a mixed gas thereof is used as a plasma gas for producing Ru powder having a hollow inside.
3. The manufacturing method of Ru powder according to the claim 1, wherein the atmospheric heat process is performed at 800-1200 °C for 1-5 hours.
4. The manufacturing method of Ru powder according to the claim 1, wherein the step for pulverizing powder is performed by any one selected from Ball Mill, Planetary Mill or Jet Mill.
5. The manufacturing method of Ru powder according to the claim 1, wherein the hydrogen atmospheric heat process is performed under 800-1200 °C for 1-5 hours.